MAGNETISM AND ATOMIC STRUCTURE

EDMUND C. STONER

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BY

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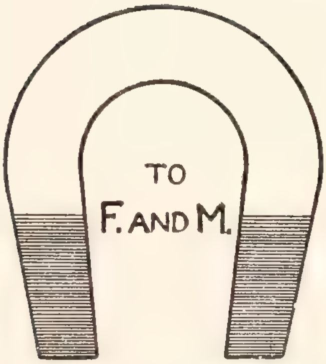

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PREFACE

IN this book an account is given of magnetic phenomena, and of the attempts made to interpret them in terms of the quantum theory which has been so successfully applied to the general problem of atomic structure. The basis of the quantum theory is still obscure, and its formulation uncertain, and there are many gaps and difficulties in its development. Some of these become especially prominent in magnetism, which was for long regarded rather as a stumbling-block for the quantum dynamical atomic theory. Closer consideration, however, shows that it actually yields remarkably strong support for it. It seems certain that the further study of magnetic phenomena, instead of undermining the quantum theory, will greatly strengthen it as a coherent whole, and will possibly throw light on its essential significance. For this reason magnetism has at present an immediate importance much wider than that arising from its own intrinsic interest.

Many investigators of magnetic problems have quite rightly insisted that any general theory is inadequate which does not consider magnetism; but they have sometimes forgotten that magnetic theories are also useless unless they link on with well-established general theory. For this reason it has seemed unfruitful to follow up a great number of views which have been put forward, interesting and ingenious though they may be in themselves.

Even if it were possible, it would be of doubtful value to give anything approaching a complete account of the enormous mass of work which has been done even in restricted regions of magnetic investigation. The general method adopted, therefore, has been to give tolerably complete outlines of representative researches, and to base discussions on these. Prominence is given to work which is thought to be of most importance and lasting value; but the selection involved is necessarily arbitrary. To obtain a clear idea of the details of particular investigators' experimental methods, or of their theoretical views, the only ultimately satisfactory way is to consult their original papers.

Although the treatment is selective rather than exhaustive, it is hoped that it is sufficiently comprehensive to give the reader a general and balanced account of the present state of the subject, and to enable him to follow its subsequent development. It may also serve as an introduction to those embarking on research in the many fields which magnetism offers.

As far as possible, the book is intended to be complete within the range to which it restricts itself. The treatment is largely semi-historical, and to a certain extent recent developments in outlook are reflected in passing from the earlier to the later chapters. It has not been possible to discuss some of the latest interpretations of quantum kinematics and dynamics, but it is perhaps too early to estimate the influence which these may have on magnetic theory.

The book is a supplement to ordinary works on magnetism, and subjects which are treated adequately in them, such as the general phenomena of ferromagnetism, are passed over or only referred to very briefly. Also, it seemed unnecessary to develop from first principles all the formulæ which are involved, when this is done in standard treatises.

Although referred to in the references, I would like to mention specially, as having been invaluable in the preparation of this book, Debye's article on magnetism in the *Handbuch der Radiologie*; the Report of the National Research Council on *Theories of Magnetism*; Sommerfeld's *Atombau und Spektrallinien*; and Jeans' *Electricity and Magnetism.*

The references at the ends of the chapters are admittedly selective, but it is believed that they will be more useful for this reason. The existence of *Science Abstracts* makes the attempt to compile a complete (and unwieldy) bibliography as unnecessary as it would be laborious. For the earlier work, some of the classical papers are specifically referred to, and bibliographical sources are given. To recent work falling within the range with which the book is more particularly concerned the references are believed to be reasonably complete. A list of the most recent papers is given in the appendix.

I cannot adequately acknowledge all the help, direct and indirect, that I have received. I would like, however, especially to thank Professor Whiddington for his kind and sympathetic encouragement, advice and continuous interest. Such value as the book may have is largely the result of friendly discussion with those with whom I worked at the Cavendish Laboratory (among them I must mention particularly Dr. Kapitza) under the inspiration of Professor Sir Ernest Rutherford; and with members of the Physics and Chemistry Staffs at Leeds. I am indebted to Mr. L. G. Stanton for the diagrams. In reading the proofs I have had help from my father, and in preparing the manuscript and compiling the index from Mrs. Fletcher.

I cannot, perhaps, end this preface better than with an expression of the hope, so much more necessary here than in its original context, " that the defects I have been guilty of upon this difficult subject may be not so much reprehended as kindly supplied, and investigated by new endeavours of my readers."

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APRIL, 1926

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MAGNETISM AND ATOMIC STRUCTURE

CHAPTER I

HISTORICAL INTRODUCTION

1. Early History

MAGNETIC and electric phenomena must now be regarded simply as different aspects of the properties of electric charges in motion or at rest. It is, however, barely a century since those discoveries were made which resulted in a clear understanding of the relation between electricity and magnetism, linking them together in the wider science of electromagnetism. Till then the two subjects developed independently, and as far as the simpler phenomena are concerned, they may still frequently be treated without reference to each other.

The science of magnetism grew from the observation of the attractive power of lodestone for iron, and of electricity from that of the attractive power of rubbed amber for light bodies. It is interesting to notice that the two earliest observed electromagnetic phenomena—permanent magnetism and frictional electricity—are among those which have longest defied completely satisfactory explanation.

Legend attributed the discovery of magnetite to a Cretan shepherd, who was so strongly drawn to the earth by his iron-tacked sandals and iron-tipped crook, that he dug to find the cause. Many fables sprang up round the remarkable stone—of magnetic mountains which drew the nails from distant ships, and of magnetic domes supporting iron statues in mid-air. There was, however, a certain amount of positive knowledge. Socrates and Pliny refer to the fact that magnetite can impart its attractive power to iron, as shown by the long chains of "Samothracian rings." Magnetic induction was dimly realized.

The name "magnet," according to Lucretius (95–52 B.C.), was derived from Magnesia, the region in Asia Minor where magnetite occurred. A fairly good idea of the Romans' knowledge of magnetism can probably be obtained from the discussion on the subject in *De Rerum Natura.* Lucretius was less interested in phenomena themselves, though he frequently describes them with vivid imaginative power, than in finding non-supernatural explanations of them ; and he applied the atomic theory with great speculative skill for this purpose. The magnet was supposed to give off an exhalation of fine particles, which smote the air asunder, so that an iron ring, pushed by the buffetings of the air molecules beyond and those in its own substance, would rush towards the void space. Iron is specially affected owing to its peculiar nature :

> " And naught there is
> That of its own primordial elements
> More thoroughly knit or tighter linked coheres
> Than nature and cold roughness of stout iron."

A definite advance is, however, recorded, in that repulsive phenomena had been observed :

> " I've seen
> Those Samothracian rings leap up,
> And iron filings in the brazen bowls
> Seethe furiously, when underneath was set
> The magnet stone."

This was difficult to explain, but Lucretius rose to the occasion. With brass between the iron and the magnet, fine particles emanating from the brass fill the pores in the iron ; no longer can the tide from the magnet swim through ; it dashes and beats against the iron's fabric, and the iron is repelled.

The Greeks and Romans never advanced beyond vague qualitative knowledge and speculation—speculation frequently showing remarkable insight, but, being unchecked by experiment, of little permanent scientific value. The idea of carrying out an experiment to find a definite answer to a definite question as to how nature behaved had not arisen.

There are vague references to south-pointing chariots in China in very ancient times, but that these indicate that the compass was known is very doubtful. The first really definite statement as to a land compass dates from the eleventh century ; and declination had then been noted. In Europe the mariner's compass—first mentioned by Neckam of St. Albans in the twelfth century—was in use at the time of the Crusades. It is actually doubtful whether the knowledge of it was carried from East to West by way of Arabia or in the opposite direction, though it seems certain that the more convenient methods of mounting originated in Europe. In early times the compass consisted simply of a magnetic needle in a splinter of wood floating in water.

With Peter Peregrinus of Maricourt magnetism enters on a new phase. It definitely begins as a science. Of Peregrinus little is known beyond what is recorded by Roger Bacon, who met him in Paris and had a great admiration for him. "What others strive to see dimly and blindly, like bats in twilight, he gazes at in full light of day, because he is a master of experiment. Through experiment he gains knowledge of natural things." The discoveries in magnetism are set forth in a letter (1269) to Sigerius of Fontancourt, a soldier friend. Peregrinus constructed a globe of lodestone and traced on it the lines along which a magnetic needle tended to set itself. He was thus led to the invention, by analogy, of the term magnetic "poles," the poles being the regions in which the magnetic power is concentrated. He found that the fragments of a broken magnet behave as magnets, isolated poles not occurring. He differentiated the two kinds of poles, and showed that unlike poles attracted each other, and like repelled. He found that a strong magnet reversed a weaker one. He designed a compass with a pivoted needle and graduated scale. With Peregrinus the experimental method as applied to magnetism came into being.

For some three hundred years little progress was made, but in William Gilbert of Colchester (1540–1603), Peregrinus had a worthy successor, one who embodies the essential spirit of the Renaissance, and is indeed one of the outstanding geniuses of science of all time. Gilbert was a doctor by profession; he became court physician to Queen Elizabeth, who gave him a pension which enabled him to prosecute his scientific researches. In 1600 was published his great work on Magnetism—*Physiologia Nova, seu Tractatus de Magnete, Magnetisque Corporibus, et de magno magnete tellure.* He does not conceal his hearty scorn of those whose opinions are based on hearsay, tradition and speculation. The book, containing the foundations of magnetic science, is dedicated not to "lettered clowns, grammatists, sophists, spouters," but "to you alone, true philosophers, ingenuous minds, who not only in books but in things themselves look for knowledge."

The refutation of the unfounded speculations, and of the ridiculous superstitions, medical and otherwise, which had grown up in connection with the magnet, was a necessary step in Gilbert's work, and one which was frequently only possible by painstaking experiment; but the positive achievements are of greater importance. The earlier results of Peregrinus were refined and extended. Electric and magnetic forces were clearly differentiated. Bodies which could be electrified by friction, of which Gilbert showed there was a large class, " electrics," attracted everything ; the lodestone, however, which required no frictional stimulus, attracted only magnetizable substances ; the attraction was unaffected by the interposition of screens of paper or cloth ; and there was an orientating tendency. Observations were made on the effect of heat on the iron, which when red hot ceases to be attracted, but reverts to its ordinary state when cooled down. Perhaps Gilbert's main discovery was that the earth itself behaves as a great magnet. This conception, which replaced the views that a magnetic attractive point existed " beyond the heavens " or in the stars, was capable of explaining the then known terrestrial magnetic phenomena with beautiful and coherent simplicity, and Gilbert's " terrella " of lodestone enabled the effects to be experimentally illustrated in a most pleasing and satisfying manner.

As to hypothesis on the cause of magnetic action, since matter cannot act where it is not, Gilbert, perhaps inspired by the medical doctrine of humours, favoured an effluvium theory, which, in spite of its crude vagueness, was for long not devoid of usefulness.

2. From Gilbert to Poisson

Gilbert's book not only forms an epitome of what was known up to his time, but, with his discoveries, for almost two hundred years afterwards. *De Magnete* was too much in advance of its time, and too severe, to be highly appreciated ; and some of the wilder cosmological conclusions may have brought it into disfavour. It was soon forgotten. In terrestrial magnetism there was considerable progress ; dip and variations of declination had been discovered, and these were investigated more fully, valuable observations being made ; theories, mostly less valuable, were elaborated. In magnetism proper, however, beyond the rediscovery of Gilbert's discoveries, there is little to record, until experiments were undertaken which resulted in the passing of the science from the qualitative to the quantitative stage.

The credit for the first step in this direction should probably be given to John Mitchell (1724–93). He was the first inventor of the torsion balance ; and the method for determining the density of the earth which was used by Cavendish was suggested by him. The principles of magnetic theory, arrived at from his experiments, were put forward in *A Treatise of Artificial Magnets* (1750) not long after he had taken his degree at Cambridge. Gilbert's views were taken over and extended by the observation that each pole of a magnet attracted or repelled exactly equally, at equal distances, in every direction, the magnetical attraction and repulsion being exactly equal to each other. This was quite at variance with prevailing ideas. Mitchell further made the fundamental discovery, based on his own and other observations, that " the Attraction and Repulsion of Magnets decreases, as the Squares of the distances from the respective poles increase." This was confirmed by the work of John Robison (1739–1805), who used magnets in the form of thin rods with spherical end pieces. The localization of polarity simplified the calculations, and experiment gave the result that the force varied as an inverse power of the distance equal to 2·06.

Coulomb (1736–1806), after a career in the army, and as an engineer, occupied himself with scientific research, and from a study of torsional elasticity, was led to the application of the torsion balance to the accurate investigation of the forces between electric charges and magnetic poles. Mitchell's result was confirmed. In a comprehensive series of memoirs, Coulomb elaborated theories of electric and magnetic action.

As was natural, developments in theories of electrostatics and magnetism proceeded simultaneously, mutually influencing each other; and attempts were made to explain the actions in terms of mechanisms of similar kinds. Descartes' vague vortex hypotheses early fell out of favour, though not conclusively disproved till Coulomb's time. The idea of effluvia emanating from electrified or magnetized bodies, but always connected to them and eventually returning, was incompatible with the facts of electric conduction. It was succeeded by the one and two fluid theories, and the choice between them had to be made rather on æsthetic than definite experimental grounds. The one-fluid theory, favoured by Franklin for electricity, was applied with considerable success by Æpinus (1724–1802) to magnetic phenomena in his *Testamen Theoriæ Electricitatis et Magnetismi* (1759). The particles of the magnetic fluid were supposed to repel each other and attract the particles of iron, which themselves exerted mutual repulsion. The fluid moved through the pores of iron or soft steel with little obstruction, which increased as the steel increased in hardness. The theory of two magnetic fluids, boreal and austral, was, however, preferred by Coulomb. He showed that electric phenomena could be explained in terms of two fluids, vitreous and resinous, or positive and negative, the parts of the same fluid repelling each other according to the inverse square law, and attracting the parts of the other fluid according to the same inverse square law. A similar conception was applied to magnetism, with an important addition, necessary because the two magnetic fluids, unlike the electric, cannot be obtained separately. Coulomb supposed that the magnetic fluids were permanently imprisoned within the molecules of magnetic bodies; magnetization consisted in the separation of the two fluids to opposite ends of each molecule.

At the end of the eighteenth century, then, the main features of magnetostatic phenomena, for iron at least, had been discovered; and the actions were explained in terms of a two-fluid theory, combined with action at a distance according to an inverse square law; but mathematical development of the theory had scarcely begun. Mathematical analysis had, however, grown rapidly since the time of Newton and Leibniz, and it began to be applied to physical problems. Poisson (1781–1840) put the crown on Coulomb's work in two remarkable memoirs dealing with electrostatic (1812) and magnetic theory (1820). He used Coulomb's views as the basis of the treatment, but the results are to a large extent independent of the actual assumptions (though of course dependent on the experimentally determined inverse square law) and remain a correct mathematical formulation of the quantitative aspects of magnetic action. He obtained expressions for the magnetic force due to a magnet of any form in terms of a volume and surface integral of functions involving the intensity of magnetization; calculated the forces inside cavities in magnetic bodies; and also discussed the question of induced magnetism.

Poisson's treatment was extended and largely freed from arbitrary assumptions by later investigators, notably Green and Kelvin; but in essentials it forms the basis of the modern statistical theory of magnetism.

3. Electromagnetism

By a happy coincidence, this culminating point in the development of magnetism as a separate science was reached just when the first discoveries were being made which connected it up with electricity. In 1819 Oersted (1777–1851) found that a compass needle was deflected when in the neighbourhood of a current-bearing wire placed parallel to it. The discovery was made at the end of a lecture, in a sense by accident; but it was an accident that was well deserved. As far back as 1807 Oersted had been seeking for some electric action on a magnetic needle. He was "a man of genius, but a very unhappy experimenter"—as is, indeed, not uncommon. A transverse force, moreover, had never been anticipated. The discovery once made, Oersted fully realized its significance, and carried out confirmatory experiments on a larger scale. He attributed the action to a "conflict of electricity," not confined to the conductor, but dispersed in the surrounding space. This "conflict," performing circles round the wire, penetrated non-magnetic bodies, but the particles of magnetic bodies resisted its passage. The stress on the physical picture is of interest at a time when action-at-a-distance views were prevalent. Oersted himself did not determine the quantitative laws, but the communication of his discoveries to the French Academy gave a strong incentive to further research. The work of Arago, Biot and Savart, and Ampère showed that there was mutual magnetic action between currents and magnets, and currents and currents. The quantitative laws were determined in special cases. In 1825 Ampère (1775–1836) dealt comprehensively with the whole subject in one of the most celebrated memoirs in history of physics, "perfect in form," Maxwell says, "and unassailable in accuracy."

Ampère avoids the introduction of hypothetical fluids and æthers (though he admits that they may be necessary in more fundamental explanations) and, adopting the action-at-a-distance standpoint, interprets all the phenomena in terms of equal and oppositely directed forces between pairs of particles. Working directly from the experimental observations, and generalizing, he shows that the action between current circuits is consistent with the view that the force between two current elements is proportional to the lengths, and the current strengths, and, in the simple case where the elements are at right angles to the line joining them, varies inversely as the square of the distance between them. Ampère further introduces the extraordinarily useful conception of the magnetic shell; and shows that a current circuit is equivalent in its magnetic effects to a normally magnetized shell of arbitrary form whose boundary coincides with the circuit.

Faraday (1791–1867) had none of the mathematical skill which distinguished so many of the contemporary continental physicists; but his wonderful insight and imagination, and his powers of visualization, combined with untiring patience and trust in facts, resulted in a life of discovery which is almost unparalleled. In 1831 Faraday discovered electromagnetic induction; undoubtedly it was his visualization of actual physical magnetic lines of force arising from magnets (or equivalent circuits) which enabled him in no more than ten full and hectic days of research between August and November virtually to unravel all the essential features of the phenomenon. "The quantity of electricity thrown into a current," he states, "is directly as the number of curves intersected." Shortly afterwards, full of the joyous satisfaction of discovery, he writes to his friend Phillips, "For once in my life I am able to sit down and write to you without feeling that my time is so little that my letter must of necessity be a short one." He gives a brief summary of the paper he is writing: "There is a bill of fare for you." It is unfortunately not possible to linger over personal details about investigators, and as the central subject-matter of this book is being approached, the historical threads must be gathered more closely together.

The laws of electromagnetic induction were further investigated and clearly formulated by workers in America (particularly Henry) and on the Continent. The making of the science of electromagnetism into a comprehensive whole is the work of another giant, Maxwell (1831–79) who, somewhat as Poisson followed Coulomb, and Ampère Oersted, followed Faraday and translated his views into mathematical language. The famous treatise, in which Maxwell's work is gathered together, though much of it is presented in a new manner, appeared in 1873. Faraday was never content with action-at-a-distance explanations, but interpreted the observed electric and magnetic forces in terms of stresses and strains in the medium. Free space was a medium in that it could support these strains which were pictured as occurring along or at right angles to tubes of force. Maxwell gave these views precise mathematical expression. He spent much ingenuity in devising mechanical models of the æther, but the final equations can be looked upon simply as generalizations of the observed experimental results. The equations virtually state the electric force due to charges, and the magnetic force due to poles; and the electric force arising from changing magnetic field (embodying Faraday's discovery) and the magnetic force arising from changing electric field. This last did involve extrapolation beyond experiment. Experiment had shown what were the magnetic forces arising from currents; but this was not sufficiently general; and Maxwell virtually guessed—and the guess has been abundantly verified—that as far as magnetic effects were concerned an electric conduction current was equivalent to a change in the electric displacement or polarization. (This is consistent with the supposition that Ampère's laws as to the action between current elements were valid for the elements themselves, and not merely when integrations were made over whole circuits.)

Maxwell thus derived four sets of equations which for free space assumed a particularly simple and symmetrical form; and from them he deduced that electromagnetic disturbances should be propagated with a finite velocity c which could be deduced from the ratio of the measured values of any electrical or magnetical quantity in electrostatic and electromagnetic units. (The electromagnetic unit of capacity is c^2 times the electrostatic; measurement of a capacity in both systems of units leads to a value of c.) The value of c deduced electromagnetically comes out within the limits of error the same as that derived directly from experimental determinations of the velocity of light or electromagnetic waves. It is unnecessary to give an account of Hertz's subsequent verification of Maxwell's predictions by the experimental production of electromagnetic waves, and of the way in which this work laid the foundations of modern wireless.

4. Atomic Magnetism and the Electron Theory

The phenomena of magnetization also occupied Maxwell's attention. Poisson had supposed that when iron became magnetized under the influence of a field the underlying mechanism was the separation of the austral and boreal fluids to opposite ends of the molecule. While an analogous explanation of dielectric polarization might be considered satisfactory, the high values of the induction observed for iron rendered the magnetic hypothesis untenable; moreover it was unable to account, in any simple manner, for saturation phenomena. Ampère, in a flash of inspiration, was led from a consideration of the equivalence of magnets and current circuits, to the suggestion of "molecular currents," which gave rise to permanent molecular magnets. These were ordinarily orientated at random, but when a field was applied, tended to set in the field direction. At the time the idea was highly speculative. In 1845, in the course of investigations on the relation between magnetism and light, Faraday discovered that magnetic properties were not confined to the iron group of elements, but that all substances were weakly magnetic, and could be divided into two classes of para- and dia-magnetics, according as to whether they tended to set themselves along the field, like iron, or at right angles to it. (Unknown to Faraday, the repulsion of bismuth by a magnet had been observed long before by Bruygmans in 1778.) Faraday rather favoured a "conduction" theory of magnetism, paramagnetics possessing high conducting power, so that the magnetic lines of force tended to crowd into them, and diamagnetics low, the lines of force tending to avoid them.

The "polarity" view was developed by Weber (1854). In diamagnetics molecular currents were supposed to be induced in the opposite direction to those giving rise to the field. Paramagnetics had molecules which behaved as permanent magnets owing to circulating currents. To account for the non-attainment of saturation in small fields Weber supposed that there was a constraint on the rotation of the magnets due to a magnetic field along the initial direction of their axes. This hypothesis was unable to explain residual magnetism ; and Maxwell modified it by supposing that there were other possible positions of equilibrium. This gave results in qualitative agreement with experiment, but it was artificial. Ewing has shown (1890) that the general phenomena of hysteresis and residual magnetism can be satisfactorily accounted for by a consideration of the constraints the neighbouring molecules exert on each other due simply to the fact that they are magnets. This view he has developed and extended with great success. Maxwell also considered diamagnetism, and obtained for the susceptibility an expression involving the self-inductance of the molecular circuit. Further progress along these lines required a justification of the speculative idea of molecular currents, and much more detailed knowledge of the intimate structure of matter was necessary before this could be given, as it eventually was, on the basis of the electron theory.

The idea of electrons, discrete elementary charges, as theoretically necessary, arose some time before electrons were actually discovered. According to Maxwell's theory the velocity of light in a medium should vary inversely as the square root of the dielectric constant. This was approximately true for many substances, but for others there were wide discrepancies. It was found that these could be very satisfactorily accounted for, in a general manner, if it was supposed that there were in the medium discrete electric charges, bound to the molecules or atoms by quasi-elastic forces such that their natural period was of the same order as that of the incident radiation. Although there were early and vigorous speculations, the main credit for the development of a coherent and consistent electron theory is undoubtedly due to H. A. Lorentz, one of the greatest of theoretical physicists. A complete explanation of electromagnetic phenomena was sought in terms of " æther " and discrete positive and negative electric charges.

5. The Electron. Further Magnetic Discoveries

The fascinating history of the actual discovery of the real electron of which the theorist had dreamed, is well known. Associated with the names of Crookes, Schuster, Lenard, Wien and others, it culminated in the work of J. J. Thomson just before the opening of the present century. Subsequent investigation has confirmed the view that the negative electron has a mass some 1800 times less than the hydrogen atom, whereas positive charges are always associated with masses of atomic magnitudes. In particular, the magnificent researches of Millikan have shown that the charge on the electron is constant, forming an ultimate fundamental unit.

As to positive charges and the masses associated with them, it will be sufficient to mention that positive ray analysis, as developed by Aston, has shown that the masses of all atoms, to a close approximation, are integral multiples of that of hydrogen; that in an atom, as shown by Rutherford from his experiments on α-ray scattering (1911), the positive charge is associated with a small concentrated nucleus; and that the nuclei of atoms have positive charges, as may be deduced in particular from X-ray spectra, equal to their atomic number. Atoms, then, consist of a nucleus, built up of hydrogen nuclei (protons) and electrons, with electrons circulating round it, equal in number, in a neutral atom, to the resultant positive nuclear charge. It is direct experiment which has led to the discovery of protons and electrons as fundamental entities; and it is in terms of the properties of these, at rest or in motion, alone and interacting, that the attempt must be made to explain physical phenomena.

It remains to review briefly the progress of specific magnetic work during these years; and to point out the difficulties which have arisen in connection with classical electromagnetic theory, and which have necessitated the introduction of those new conceptions, as yet so incompletely understood, which are embodied in the theory of quanta. That there was a close connection between magnetism and light was held strongly by Faraday; and in 1845 he made another great discovery—of the rotation of the plane of polarization of light in passing through substances placed in a magnetic field. In 1871 Kerr discovered polarization changes accompanying the reflection of light from the poles of a magnet. In 1896 Zeeman observed an effect which Faraday had sought unsuccessfully—the modification of the frequency of light from a source placed in a magnetic field; a spectral line was split into components which were differently polarized with respect to the direction of the field. Some lines (those belonging to singlet series) were split up, as observed transversely to the field, into triplets. A beautifully satisfactory explanation of this "normal" effect was given by Lorentz on the basis of classical electron theory; but the more complicated resolutions defied theoretical interpretation.

One of the most fruitful researches in the history of magnetism was that of P. Curie (1895), who investigated the dia- and paramagnetic susceptibilities of many substances and their variation with temperature. He found that while diamagnetism was usually independent of temperature, paramagnetic susceptibility, over wide ranges, was very approximately inversely proportional to the absolute temperature—a result embodied in the law bearing his name. This led to important theoretical developments, and in 1905 Langevin published a classical paper which lies at the foundation of most modern work. Molecular currents could now be regarded as due to electrons circulating in the molecules. The general explanation of the magnetic effects was the same as before, but rendered somewhat more precise by the definite physical picture; and by applying statistical treatment to investigate how the orientation of the molecules under the influence of a field would be affected by the thermal motions, Langevin obtained an expression for the variation of paramagnetic susceptibility with temperature which, for small fields, reduced to Curie's law. Not long after, Weiss (1907) introduced the conception of intrinsic molecular fields, proportional to the intensity of magnetization acquired; the modification produced in Langevin's expressions by this enabled many of the phenomena of ferromagnetism to be satisfactorily explained, as well as some of the deviations from Curie's law shown by many paramagnetics. It had now become possible, on the basis of these theories, to calculate the atomic and molecular magnetic moments. In the course of his investigations on ferromagnetics, Weiss was led to the conclusion (1911) that these were all integral multiples of a unit "magneton." While later work has shown that the original view requires profound modification, it undoubtedly has elements of truth; it has stimulated research, and has had immense value in enabling magnetic measurements to be clearly presented and co-ordinated.

6. The Quantum Theory

There was of course a difficulty in the simple electron theory of magnetism in that electrons rotating in orbits should radiate, according to classical theory. For this and other reasons there have been many abortive speculations centring round the view that the electron, even when not rotating in an orbit, is also a magneton—consisting, that is, of a swirl of electricity with the properties of a magnet. These views, frequently ingenious, and of mathematical interest, will not be followed up here, for they have been singularly unfruitful; and the difficulties which gave rise to them are part of a much larger problem which is being resolved in a different manner.

Towards the end of the nineteenth century the classical electromagnetic theory seemed in its main lines unassailable; but " clouds " were beginning to attract attention. The æther could not be regarded as a material medium; but none the less electricity and magnetism could be treated as subject to generalized dynamical laws; in particular it was possible to work out the distribution of energy between matter and radiation in equilibrium in an isothermal enclosure; the classical result—that the whole energy should tend to concentrate in the ætherial vibrations of short wave-length—was in complete disaccord with experiment. In 1900 Planck put forward the revolutionary view that material " resonators " could only possess (and hence also only gain or lose) energy in integral numbers of discrete units, quanta, the magnitude of these quanta being proportional to the frequency of the radiation emitted or absorbed (the ratio of the energy to the frequency being Planck's constant). This was the origin of the quantum theory. It enabled Planck to account completely for the observed distribution of energy in the temperature radiation spectrum. In 1905 Einstein gave a quantum explanation of the photoelectric effect based (though not of necessity) on the assumption of radiation being propagated by " light darts." Shortly afterwards, the theory was applied by Einstein, Nernst and Lindemann, and Debye, with great success, to the interpretation of the observations on specific heats, particularly at low temperatures.

The basis of the present-day outlook on the quantum theory was laid in 1913 by Niels Bohr in his paper on the constitution of atoms and line spectra, in which were considered especially hydrogen and ionized helium. The treatment is essentially based on the Rutherford picture of the atom, and on two fundamental postulates. According to the first, electrons in the atom rotate round the nucleus in " stationary " stable orbits, without radiating; these possible states are fixed by supposing that the angular momentum can only assume certain discrete values, simply related to integral multiples of Planck's constant. The atom is stable. The possible electron orbits and the corresponding energies of the atom can be calculated, at least in simple cases. The transition of an atom from one possible stationary state to another (the details of this process are left completely undefined) is accompanied by the emission or absorption of monochromatic radiation of frequency, according to the second postulate, given by the energy difference divided by Planck's constant.

From a magnetic point of view the most important feature of the theory is the fact that the angular momentum of an electron can only assume discrete values; for the magnetic moment is simply related to the angular moment ; and the theory therefore implies that atomic magnetic moments must all be multiples of a fundamental unit. This unit is five times as great as the Weiss magneton. It will be seen later that there is now a considerable body of evidence, as deduced from experimental measurements, that the Bohr theoretical magneton possesses real physical significance.

For an explanation of the Zeeman effect in terms of the quantum theory it is necessary to suppose that atoms, with their magnetic electron orbits, orientate themselves in definite directions in an applied magnetic field, even when this is very small. This surprising conclusion has been confirmed by direct experiments on the deviation of a stream of atoms in a non-homogeneous field by Gerlach and Stern. The association of angular with magnetic moment suggests that the acquirement of magnetization should be accompanied by rotational impulse ; and that rotation should give rise to magnetization—views first developed clearly by Richardson in 1908. This has been experimentally verified ; but the ratio of the two effects, the magnetic to the mechanical, has turned out to be exactly twice that anticipated on the basis of the usual theory. The significance of this "gyromagnetic anomaly," which is undoubtedly of great importance, is not yet understood, though it has been brought into relation with difficulties arising in the quantum treatment of the Zeeman effect.

The immense amount of work that has been done in the last twenty or thirty years on magnetism has made it possible to trace back the phenomena observed to the atom itself. The magnetic properties of individual atoms may, to a certain extent, be deduced ; and the attempt may be made to link these up with other characteristics. Working in the opposite direction, synthesizing, a clearer idea of mass magnetic phenomena may then be obtained. Moreover, a study of the magnetic properties may throw light on many obscure features in the theory of the atom ; looked at from another point of view, the quantum theory may assume new significance ; and the solving of many of the problems of radiation will be helped by the key provided by a study of how radiation phenomena are affected by magnetic influences.

Throughout the history of magnetism, speculation, experiment and theory have all played their part. While untrammelled speculation has been of little service, speculation guided and checked by experiment has been of the utmost value ; and theory and experiment have both progressed most vigorously when brought into close relation to each other. It is the insight and genius of the few—the great scientific artists—which have made clear the straight paths through the chaos of unco-ordinated phenomena ; they have conceived and revealed a design running through the whole ; but it is the untiring skill and patient labour of the many that have given to their visions significance and reality.

REFERENCES. I

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CHAPTER II

CLASSICAL ELECTROMAGNETIC THEORY

1. Preliminaries

IN the present chapter the main results of classical electromagnetic theory will be stated and developed in so far as they will be useful in their application to magnetic phenomena. The outline given is principally intended for reference later.

The equations will be mainly presented in vector form, though with Cartesian interpolations. The vector notation is convenient and concise, but independently of this, it is the natural one to adopt in dealing with electromagnetic phenomena; directed quantities have to be considered, and the mathematical symbols of vector analysis give a simple and direct representation of the physical conceptions. The Cartesian procedure of splitting up an electric force, for example, into x, y and z components, is at best very artificial. It is, however, frequently useful, and when desired, it is a matter of but slight difficulty to transform the vector notation into the sometimes more familiar Cartesian form.

The notation adopted will be that advocated by Coffin. Vectors will be distinguished where necessary by being printed in thicker type. Vector products will be denoted by a small cross, scalar by a dot. Thus $\mathbf{A} \times \mathbf{B}$ is a vector at right angles to $\mathbf{A}$ and $\mathbf{B}$, and equal in magnitude to $AB \sin \theta$, θ being the angle between $\mathbf{A}$ and $\mathbf{B}$; $\mathbf{A} \cdot \mathbf{B}$ is a scalar equal to $AB \cos \theta$. A subscript $_1$ will be used to denote the unit vector in any direction (as $\mathbf{A}_1$, $\mathbf{r}_1$); $\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$ being used, however, for unit vectors in the x, y, z directions.

The vector operator $\boldsymbol{\nabla}$, which is of wide application, may be defined as

$$\boldsymbol{\nabla} \equiv \mathbf{i}\frac{\partial}{\partial x} + \mathbf{j}\frac{\partial}{\partial y} + \mathbf{k}\frac{\partial}{\partial z}.$$

It may be applied to scalar point functions, giving a vector, and scalarly and vectorially to vector point functions; the following gives various equivalent forms, and will enable the vector notation to be transformed if desired.

$$\nabla\phi \equiv \text{grad }\phi$$

—a vector giving the rate of change of ϕ in the direction in which it changes most rapidly.

$$\nabla\cdot\mathbf{A} \equiv \text{div }\mathbf{A} \equiv \frac{\partial A_x}{\partial x} + \frac{\partial A_y}{\partial y} + \frac{\partial A_z}{\partial z}$$

—a scalar.

$$\nabla\times\mathbf{A} \equiv \text{curl }\mathbf{A}$$

—a vector, whose Cartesian components are given by

$$\left(\frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z}\right), \left(\frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x}\right), \left(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}\right).$$

A number of mathematical theorems which will be useful will first be stated. Gauss's Theorem, valuable in dealing with vector functions following an inverse square law, enables the integrated solid angle subtended by elements of a closed surface at a point to be obtained in terms of the distances of the elements from the point, and may be expressed

$$\int d\omega = \iint \frac{\cos(\mathbf{rn})}{r^2} dS = \iint \frac{\mathbf{r}\cdot\mathbf{n}}{r^3} dS = 4\pi \quad . \quad . \quad (1)$$

$$\text{(O inside S)}$$
$$= 0$$
$$\text{(O outside S)}$$

Here $d\omega$ is the elementary solid angle subtended by dS at a distance r from O, and $\mathbf{n}$ the unit normal to dS.

The divergence theorem enables surface integrals (taken over a closed surface) to be expressed as volume integrals (taken over the whole volume). If $\mathbf{A}$ is a general vector function of position

$$\iint_S \mathbf{n}\cdot\mathbf{A}\,dS = \iiint_v \nabla\cdot\mathbf{A}\,dv = \iiint_v \text{div}\mathbf{A}\,dv \quad . \quad . \quad . \quad (2)$$

If l, m, n are the direction cosines of the normal to the surface, A_x, A_y, A_z the components of $\mathbf{A}$, this may be expanded in Cartesian form—

$$\iint_S (lA_x + mA_y + nA_z)dS = \iiint_v \left(\frac{\partial A_x}{\partial x} + \frac{\partial A_y}{\partial y} + \frac{\partial A_z}{\partial z}\right)dv \quad (2.1)$$

By Stokes' Theorem the line integral of a vector taken round a closed curve may be transformed into a surface integral of a derived vector taken over any surface bounded by the curve

$$\int_s \mathbf{A}\cdot d\mathbf{s} = \iint_S \mathbf{n}\cdot\nabla \times \mathbf{A}\,dS = \iint_S \mathbf{n}\cdot \operatorname{curl} \mathbf{A}\,dS \quad . \quad . \quad (3)$$

or, in Cartesian form,

$$\int_s \left(A_x\frac{dx}{ds} + A_y\frac{dy}{ds} + A_z\frac{dz}{ds}\right)ds$$

$$= \iint_S \left\{l\left(\frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z}\right) + m\left(\frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x}\right) + n\left(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}\right)\right\}dS \quad (3{\cdot}1)$$

While the transformation from a line to a surface integral is unique, the transformation in the opposite direction yields a general solution containing arbitrary terms. Suppose it is desired to transform the surface integral

$$\iint \mathbf{n}\cdot\mathbf{F}\,dS \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3{\cdot}2)$$

into a line integral of the form

$$\int \mathbf{G}\cdot d\mathbf{s} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3{\cdot}3)$$

a general solution is

$$\int \mathbf{G}\cdot d\mathbf{s} = \int\left[\iint \mathbf{n}\cdot\mathbf{F}\frac{dS}{ds}ds\right] + \int \frac{d\chi}{ds}ds \quad . \quad . \quad (3{\cdot}4)$$

so that χ is only subject to the limitation $\int \frac{d\chi}{ds}ds = 0$. (As will readily be seen on inspection of (3) the addition of a term $\mathbf{A}'$ to $\mathbf{A}$ will not affect the integrals obtained if $\int \mathbf{A}'\cdot d\mathbf{s} = 0$.) In order that (3·3) may be transformed into the (3·2) form a necessary condition is that $\nabla\cdot\mathbf{G} = 0$.

2. The Equations for Free Space

The fundamental equations for the electromagnetic field in the form which they assume for free space may now be considered. Let **E** (components **X**, **Y**, **Z**) denote the electric, and **H** (components α, β, γ) the magnetic force. **E** may be defined as the force exerted on an electric charge per unit charge. A unit charge is one which exerts a force of one dyne on an equal charge at a distance of one centimetre, this being the basis of the electrostatic system of units. The electromagnetic system starts in a similar way from the definition of unit magnetic pole. In the equations **E** is measured in electrostatic units, **H** in electromagnetic.

$$\nabla\cdot\mathbf{E} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\nabla\cdot\mathbf{H} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\nabla\times\mathbf{E} = -\frac{1}{c}\dot{\mathbf{H}} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$\nabla\times\mathbf{H} = \frac{1}{c}\dot{\mathbf{E}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Once a relation between electricity and magnetism was established it became theoretically possible to measure any electric or magnetic quantity in electrostatic or electromagnetic units. In equations (6) and (7), c primarily denotes the ratio of the electro magnetic measure of a charge to the electrostatic. (c is most conveniently determined by measuring a capacity in the two systems, the electromagnetic being c^2 times the electrostatic unit.) From the above equations, however, it may be deduced that c should be the velocity of electromagnetic disturbances in space; experiment shows this to be true, not only for artificial electromagnetic waves, but also for radiation (including light waves) in general. Thus c may also be regarded as the velocity of light in free space.

The equations are simply generalizations from experience expressed in mathematical differential form. (4) and (5) are little more than direct consequences of definitions, though it must be remembered that the definitions were framed as being convenient for precise consideration of the phenomena concerned. (6) generalizes the experimental fact that the E.M.F. induced round a circuit is equal to the rate of change of the magnetic flux through it. Equation (7), however, at least when first put forward by Maxwell, went beyond direct experiment, and embodied what was really a happy guess; the validity of the equation rests on the fact that the results to which it leads are found to be in accord with experience. The actual experimental basis centres in the Oersted-Ampère discoveries of the magnetic effects of electric currents; for steady currents in continuous conducting media, the results may be expressed by

$$\int_{\mathbf{s}} \mathbf{H}\cdot d\mathbf{s} = 4\pi \iint_{S} \mathbf{n}\cdot\mathbf{i}\,dS \quad . \quad . \quad . \quad . \quad . \quad (7.1)$$

the integrals being taken round a closed curve, and over any surface bounded by the curve, $\mathbf{i}$ being the current density. Only when the currents are steady and continuous, however, does the current over *any* surface have a unique value. The appropriate generalization is required.

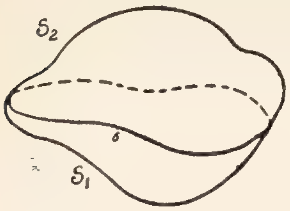

FIG. 1.

Consider a closed surface S divided by a bounding curve s into S_1 and S_2.

Let $\mathbf{i} = \frac{\varrho}{c}\mathbf{v}$

Then, in general, $\iint_{S_1} \frac{\varrho}{c}\mathbf{n}\cdot\mathbf{v}dS \neq \iint_{S_2} \frac{\varrho}{c}\mathbf{n}\cdot\mathbf{v}dS.$

Let ϱ be the density of charge enclosed within S_1 and S_2.

Then
$$\iint_{S = S_1 + S_2} \mathbf{n}\cdot\mathbf{E}dS = 4\pi\iiint \varrho dv$$

$$\iiint \frac{d\varrho}{dt}dv = -\iint \varrho\mathbf{n}\cdot\mathbf{v}dS$$

so that
$$\iint_S \varrho\mathbf{n}\cdot\mathbf{v}dS = -\frac{1}{4\pi}\iint \frac{d}{dt}(\mathbf{n}\cdot\mathbf{E})dS$$

or
$$\iint\left(\varrho\mathbf{v} + \frac{1}{4\pi}\frac{d\mathbf{E}}{dt}\right)dS = 0.$$

Thus, while $\iint \varrho\mathbf{n}\cdot\mathbf{v}dS$ has not the same value for any surface S_1, S_2 . . . $\iint\left(\varrho\mathbf{v} + \frac{1}{4\pi}\frac{d\mathbf{E}}{dt}\right)dS$ has a unique value; suggesting that the appropriate generalization of (7.1) which will apply for *any* surfaces, giving unique results, for any currents, continuous or discontinuous, is

$$\int \mathbf{H}d\mathbf{s} = 4\pi\iint \mathbf{n}\cdot\left(\mathbf{i} + \frac{1}{4\pi c}\frac{d\mathbf{E}}{dt}\right)dS \quad . \quad . \quad . \quad (7.2)$$

The content of this equation is that, as far as magnetic effects are concerned, a change in the electric "displacement," as Maxwell termed it, in the medium, is equivalent to an electric current. It may be shown that this is equivalent to assuming that Ampère's law for the magnetic force arising from currents

$\left(H = \int \frac{ids \sin \theta}{r^2}\right)$ is true not only when integrated round a complete circuit, but for each portion of the circuit separately; a result which becomes readily intelligible when a current is interpreted in terms of moving electrons, which will produce magnetic fields not merely in their immediate vicinity, but at any distance. In free space where there are no conduction currents, (7.2) reduces to the form given in the fundamental equations (7).

The differential equation satisfied by the electric and magnetic forces in free space may readily be deduced.

From (7) $\nabla \times \nabla \times \mathbf{H} = \frac{1}{c}\nabla \times \dot{\mathbf{E}} = \frac{1}{c}\frac{d}{dt}(\nabla \times \mathbf{E})$.

Now for any vector **A**,

$$\nabla \times \nabla \times \mathbf{A} = \nabla\nabla\cdot\mathbf{A} - \nabla^2\mathbf{A}$$

as may be seen on Cartesian expansion. Using this relation, and substituting from (5) and (6),

$$\nabla^2\mathbf{H} = \frac{1}{c^2}\frac{\partial^2\mathbf{H}}{\partial t^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Considering the x component

$$\frac{\partial^2 H_x}{\partial x^2} + \frac{\partial^2 H_x}{\partial y^2} + \frac{\partial^2 H_x}{\partial z^2} = \frac{1}{c^2}\frac{\partial^2 H_x}{\partial t^2} \quad . \quad . \quad . \quad (8.1)$$

Similar equations hold for **E** and its components.

(8) is the general equation for wave propagation with a velocity c, the general solution being

$$\mathbf{H} = F(r - ct) + f(r + ct)$$

the functions F and f being completely arbitrary; and appropriate forms of solution may be obtained to fit conditions. For spherical waves, for example,

$$rH = f_1(r - ct) + f_2(r + ct) \quad . \quad . \quad . \quad . \quad . \quad (9)$$

For plane simple harmonic waves travelling along the positive x axis

$$H = H_0 \sin 2\pi\left(\frac{t}{\tau} - \frac{x}{\lambda}\right) \quad . \quad . \quad . \quad . \quad . \quad (9.1)$$

where τ is the period, and $\lambda = c\tau$.

3. The Magnetic Field of Force

Since an inverse square law of attraction and repulsion forms a fundamental feature both of electrostatic and magnetic phenomena, there is a far-reaching analogy in their mathematical treatment. The difference lies largely in the questions on which most stress is laid. Magnetic poles do not occur separately, so that it is to the theory of electrostatic doublets that magnetic theory corresponds most closely; and while electrostatic "shells" are of little interest, magnetic shells, owing to their equivalence to current circuits, are of considerable importance.

It is convenient, and not without physical significance, to regard any magnet as made up of magnetic particles; the comparatively simple mathematical results for these can then be extended by integration processes.

The intensity of magnetization **I** at a point in a magnet may be defined as the magnetic moment of a small particle at the point divided by its volume; the direction being that of the magnetic axis of the particle. **I** is equal to the magnetic moment per unit volume or the pole strength per unit area. When **I** is constant throughout a body, the body is said to be uniformly magnetized.

The magnetic potential Ω may be defined by the equation

$$\mathbf{H} = -\nabla\Omega \qquad \mathrm{H}_s = -\frac{\partial\Omega}{\partial s} \quad . \quad . \quad . \quad . \quad (10)$$

In terms of the potential, Gauss's Theorem (cf. (5)) takes the form

$$\frac{\partial^2\Omega}{\partial x^2} + \frac{\partial^2\Omega}{\partial y^2} + \frac{\partial^2\Omega}{\partial z^2} = \nabla^2\Omega = 0 \quad . \quad . \quad . \quad (11)$$

which applies quite generally owing to the non-occurrence of isolated poles.

The potential at Q(x', y', z') at a distance r from a particle of moment $\boldsymbol{\mu}$ at O(x, y, z) with axis along s (direction cosines l, m, n) is

$$\Omega_Q = -\boldsymbol{\mu}\cdot\nabla\left(\frac{1}{r}\right) = +\frac{\boldsymbol{\mu}\cdot\mathbf{r}}{r^3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

$$= -\mu\left(l\frac{\partial}{\partial x'} + m\frac{\partial}{\partial y'} + n\frac{\partial}{\partial z'}\right)\left(\frac{1}{r}\right) \quad . \quad . \quad . \quad (12.1)$$

$$= +\mu\left(l\frac{\partial}{\partial x} + m\frac{\partial}{\partial y} + m\frac{\partial}{\partial z}\right)\left(\frac{1}{r}\right) \quad . \quad . \quad . \quad (13)$$

$$= \mu\frac{\partial}{\partial s}\left(\frac{1}{r}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13.1)$$

$$\mathbf{H} = -\nabla\Omega = -\nabla\frac{\boldsymbol{\mu}\cdot\mathbf{r}}{r^3}$$

$$= -(\boldsymbol{\mu}\cdot\mathbf{r})\nabla\left(\frac{1}{r^3}\right) - \frac{1}{r^3}\nabla(\boldsymbol{\mu}\cdot\mathbf{r}) = \frac{3\boldsymbol{\mu}_r}{r^3} - \frac{\boldsymbol{\mu}}{r^3} \qquad (13.2)$$

This may at once be extended to a magnetic body, giving

$$\Omega_Q = -\iiint \mathbf{I}\cdot\nabla\left(\frac{1}{r}\right)dv \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

$$= -\iiint\left(A\frac{\partial}{\partial x'} + B\frac{\partial}{\partial y'} + C\frac{\partial}{\partial z'}\right)\left(\frac{1}{r}\right)dv \quad . \quad (14.1)$$

$$= +\iiint\left(A\frac{\partial}{\partial x} + B\frac{\partial}{\partial y} + C\frac{\partial}{\partial z}\right)\left(\frac{1}{r}\right)dv \quad . \quad (14.2)$$

where A, B, C are the x, y, z components of **I**.

The differentiations in (13) and (14.2) are carried out for O (x, y, z) the position of the magnetic element; in (12.1) and (14.1) they are referred to the point Q (x', y', z') at which the potential is to be found.

If A, B, C are constant, writing V_Q for the electrostatic potential at Q due to unit density of charge throughout v, and X, Y, Z for the components of the electric force, (14) and (14.2) are mathematically equivalent to

$$\Omega_Q = -\mathbf{I}\cdot\nabla V_Q = AX + BY + CZ \quad . \quad . \quad (14.3)$$

This mathematical dodge is frequently useful. Thus the magnetic potential due to a sphere of radius a, uniformly magnetized in the x direction, since $V_Q = \frac{4}{3}\pi a^3 \times \frac{1}{r}$, is given by

$$\Omega_Q = \frac{4}{3}\pi a^3 I\frac{\partial}{\partial x}\left(\frac{1}{r}\right) = \frac{4}{3}\pi a^3 I\frac{x}{r^3} = \frac{4}{3}\pi a^3 I\frac{\cos\theta}{r^2} \quad . \quad . \quad (15)$$

A transformation due to Poisson is sometimes useful. It enables the potential to be regarded as arising from an imaginary surface and volume distribution of magnetization. Transforming (14) by Green's Theorem (2)

$$\Omega_Q = \iint\frac{1}{r}(\mathbf{I}\cdot\mathbf{n})dS - \iiint\frac{1}{r}(\nabla\cdot\mathbf{I})dv$$

$$= \iint\frac{1}{r}(lA + mB + nC)dS - \iiint\frac{1}{r}\left(\frac{\partial A}{\partial x} + \frac{\partial B}{\partial y} + \frac{\partial C}{\partial z}\right)dv \quad (16)$$

If the magnetization is uniform the second term of course vanishes.

Normally magnetized shells will now be considered. As has been mentioned they owe their importance to their equivalence to current circuits coinciding with the boundary. The shells may be supposed to have small but finite thickness t, the "strength" being given by $\phi = \mathbf{I} \cdot \mathbf{t}$. For the potential due to a shell

$$\Omega_Q = - \iint \phi \cdot \nabla \left(\frac{1}{r} \right) dS$$

$$= + \iint \phi \frac{d}{dn} \left(\frac{1}{r} \right) dS = \iint \phi \frac{\cos \theta}{r^2} dS = \int \phi d\omega \quad (17)$$

$d\omega$ being the solid angle subtended at Q by an element of the shell.

For a uniform shell, if Ω is the solid angle subtended by the whole shell at Q

$$\Omega_Q = \phi \Omega \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17.1)$$

The potential energy of a shell in a uniform field of force may be obtained by an extension of the result for a particle of moment $\boldsymbol{\mu}$ for which

$$W = \boldsymbol{\mu} \cdot \nabla \Omega = - \boldsymbol{\mu} \cdot \mathbf{H} = - \mu H \cos \theta \quad . \quad . \quad (18)$$

θ being the angle between $\boldsymbol{\mu}$ and $\mathbf{H}$.

For a shell

$$W = \phi \iint \frac{\partial \Omega}{\partial n} dS = - \phi \iint H dS = - \phi n \quad . \quad . \quad (19)$$

where n is the number of unit "tubes" of magnetic force which would cross the surface of the shell in the absence of the shell, a unit tube being one for which the product of the field strength by the cross-section is equal to unity.

If the field arises solely from a second shell

$$W = - \phi_1 n_2 = - \phi_2 n_1 \quad . \quad . \quad . \quad . \quad . \quad (20)$$

and, hence, for two shells of the same, and in particular of unit, strength, $n_1 = n_2$, an important result.

The potential energy of any magnetized body in a field, extending (18), is given by

$$W = \iiint \mathbf{I} \cdot \nabla \Omega dv = \iiint \left(A \frac{\partial \Omega}{\partial x} + B \frac{\partial \Omega}{\partial y} + C \frac{\partial \Omega}{\partial z} \right) dv \quad (21)$$

The forces may in general be obtained by differentiating the expression for the energy with reference to the direction in which the force is required.

4. Forces inside Magnetized Bodies. Induction

The concept of a force inside a magnetized body can only have definite meaning and value if the conditions under which the force is to be measured can be so specified as to lead to unique results. In order that the force may be measured experimentally or deduced theoretically it is necessary to make or imagine a cavity inside the body. The presumably rapid variations in passing from molecule to molecule necessitate that the cavity must be large compared with molecular dimensions (say 10^{-8} cm.); on the other hand it must be small compared with distances over which appreciable changes in bulk magnetization may occur (say 10^{-1} cm.). With these limitations a cavity may be chosen in two ways so that the force within it is independent of its precise shape and size, and of the position of the point in it at which the force is to be measured.

First consider a long thin cylindrical cavity with its axis in the direction of magnetization. The force within it may be regarded as arising from a surface and volume distribution of magnetization over all magnetic material (cf. (16)). The change in volume distribution owing to the presence of the cavity may be made as small as desired; its own surface distribution vanishes for the side-walls, and the force due to that on the end-walls may be made negligibly small. The force inside such a cavity, unique and independent of the precise form of the cavity, is known as the magnetic force **H** (components $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$, $\boldsymbol{\gamma}$).

In a cylindrical cavity whose length is very small compared with the end dimensions, the force will be the resultant of **H** compounded with that arising from the surface distribution on the end-walls (of amount $4\pi\mathbf{I}$). The unique force which is no longer negligible in such a cavity is known as the magnetic induction **B** (components **a**, **b**, **c**)

$$\mathbf{B} = \mathbf{H} + 4\pi\mathbf{I} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

and

$$\mathbf{a} = \boldsymbol{\alpha} + 4\pi\mathbf{A} \text{ etc.} \quad . \quad . \quad . \quad . \quad (22.1)$$

When an unmagnetized body is placed in a magnetic field, in general it becomes magnetized to a greater or less extent; the induced intensity of magnetization may be in the same direction as that of the applied field (ferro- and para-magnetics) or in the opposite (diamagnetics). For an isotropic medium, the susceptibility κ may be defined by the equation

$$\mathbf{I} = \kappa\mathbf{H} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

or

$$\mathbf{A} = \kappa\boldsymbol{\alpha}, \text{ etc.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (23.1)$$

and the permeability μ, by

$$\mathbf{B} = \mu\mathbf{H} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

From (22)

$$\mu = 1 + 4\pi\kappa \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

It will be clear, from the way in which induction is defined, that when magnetized bodies are present, it is the induction and not the magnetic force which is continuous, and to which Gauss's Theorem applies. To generalize equations (4)–(7) to apply to material media statistically as well as to free space, **B** must be substituted for **H** in (5) and (6)—but not, of course, in (7); similarly, for **E** in (4) and (7) must be substituted **D**, the electric induction, defined by $\mathbf{D} = k\mathbf{E}$ where k is the dielectric constant.

It should be noticed that the field $\mathbf{H}_i$ inside a magnetized body will differ from that outside $\mathbf{H}_e$ owing to the effect of the surface distribution of magnetism; the "depolarizing" effect may be made small by suitably choosing the shape of the body being magnetized; and in certain special cases, remembering that the induction is continuous, its value may be calculated.

In general

$$\mathbf{H}_i = \mathbf{H}_e - \mathrm{N}\mathbf{I} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

For a sphere $\mathrm{N} = \frac{4\pi}{3}$, giving

$$\mathbf{H}_i = \frac{3}{\mu + 2}\mathbf{H}_e \quad . \quad . \quad . \quad . \quad . \quad . \quad (26.1)$$

For a short cylinder

$$\mathbf{H} = \mathbf{H}_e/\mu \quad . \quad . \quad . \quad . \quad . \quad . \quad (26.2)$$

For a prolate ellipsoid, with eccentricity ε

$$\mathrm{N} = 4\pi\left(\frac{1}{\varepsilon^2} - 1\right)\left(\frac{1}{2\varepsilon}\log_e\frac{1+\varepsilon}{1-\varepsilon} - 1\right) \quad . \quad . \quad (26.3)$$

which, if the ellipsoid is much elongated, becomes

$$\mathrm{N} = 4\pi\frac{a^2}{c^2}\log_e\left(\frac{2c}{a} - 1\right) \quad . \quad . \quad . \quad . \quad (26.4)$$

where $2a$ and $2c$ are the equatorial and polar diameters. The value of N varies from ·0182 for $c/a = 50$ to ·00030 for $c/a = 500$.

5. Magnetic Vector Potential. Magnetic Energy

By Stokes' Theorem the surface integral of a vector may be expressed as a line integral of another vector taken round the bounding curve of the surface. If **B** is the magnetic induction,

and
$$\iint \mathbf{n}_1 \cdot \mathbf{B} dS = \int \mathbf{A} d\mathbf{s} \quad . \quad . \quad . \quad . \quad . \quad (27)$$

then **A** (components **F**, **G**, **H**) is known as the magnetic vector potential. It derives its value, in simplifying mathematical calculations, much as does the electrostatic potential ϕ, when used in place of the electric force **E**. Once the vector potential is determined, the magnetic field, considering free space, may be uniquely determined also from

$$\mathbf{H} = \nabla \times \mathbf{A} = \text{curl } \mathbf{A} \quad . \quad . \quad . \quad . \quad . \quad (28)$$

but in general **A** cannot be uniquely determined from **H**.

The name vector potential arises from the fact that, as a scalar potential, ϕ may be derived from a scalar function ϱ by an equation of the form

$$= \iiint \frac{\varrho}{r} dv \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

so may the vector potential **A** be derived from a vector function $\boldsymbol{\rho}$

$$\mathbf{A} = \iiint \frac{\boldsymbol{\rho}}{r} dv \quad . \quad . \quad . \quad . \quad . \quad (29.1)$$

Thus the magnetic vector potential due to currents in a circuit is given by

$$\mathbf{A} = \int \frac{i d\mathbf{s}}{r} \quad . \quad . \quad . \quad . \quad . \quad . \quad (29.2)$$

For a magnetic particle of moment $\boldsymbol{\mu}$ at x', y', z', a solution for the magnetic vector potential at x, y, z is

$$\mathbf{A} = -\boldsymbol{\mu} \times \nabla\left(\frac{1}{r}\right) = -\frac{1}{r^3} \boldsymbol{\mu} \times \mathbf{r} \quad . \quad . \quad . \quad (30)$$

(This gives $\mathbf{H} = \nabla \times \mathbf{A} = -\nabla \times \boldsymbol{\mu} \times \nabla\left(\frac{1}{r}\right)$

$$= \nabla\left\{\boldsymbol{\mu} \cdot \nabla\left(\frac{1}{r}\right)\right\} = \frac{3\boldsymbol{\mu}_r}{r^3} - \frac{\boldsymbol{\mu}}{r^3} \text{ as in 13.2).}$$

For the components

$$\mathbf{F} = -\mu\left(m\frac{\partial}{\partial z} - n\frac{\partial}{\partial y}\right)\left(\frac{1}{r}\right) = \mu\left(m\frac{\partial}{\partial z'} - n\frac{\partial}{\partial y'}\right)\left(\frac{1}{r}\right) \quad (30.1)$$

while for a magnetic shell of unit strength

$$\mathbf{F} = \int \frac{1}{r}\frac{dx'}{ds'}ds' \quad . \quad . \quad . \quad . \quad . \quad . \quad (30.2)$$

The number of tubes of induction crossing a second shell at x, y, z may then easily be calculated.

$$n = \int \mathbf{A}\cdot d\mathbf{s} = \iint\left(\frac{dx}{ds}\cdot\frac{dx'}{ds'} + \frac{dy}{ds}\cdot\frac{dy'}{ds'} + \frac{dz}{ds}\cdot\frac{dz'}{ds'}\right)\left(\frac{1}{r}\right)ds.ds'$$

$$= \iint\frac{\cos\varepsilon}{r}ds.ds' = \iint\frac{d\mathbf{s}\cdot d\mathbf{s}'}{r} \quad (31)$$

a formula which is symmetrical with respect to s and s', and which is of fundamental importance in connection with the induction between two electric circuits.

The question of magnetic energy is somewhat confusing, especially when magnetic shells and the equivalent current circuits are compared; some of the difficulties, however, which largely arise from lack of clear appreciation of the zero state from which the energy is measured, are instructive, and the results, which are of considerable importance in modern theory, must be briefly considered.

The energy W of a system of magnets a, b, c . . . is given by

$$W = \tfrac{1}{2}\Sigma\Omega(a) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

where $\Omega(a)$ is the energy of the magnet a placed in a field due to all the magnets, assuming that the energy of the magnets in their own field of force vanishes (in other words that the magnets are ultimate magnetic particles).

For a single magnetic particle $\Omega(a) = \mu\frac{\partial\Omega}{\partial s}$, and substituting $\mathbf{I}dv$ for $\boldsymbol{\mu}$, (32) may be written

$$W = \tfrac{1}{2}\iiint\left(A\frac{\partial\Omega}{\partial x} + B\frac{\partial\Omega}{\partial y} + C\frac{\partial\Omega}{\partial z}\right)dv = -\tfrac{1}{2}\iiint\mathbf{I}\cdot\mathbf{H}dv \quad (32.1)$$

This should be compared with (21) which gives the potential energy of a single magnetized body brought into a pre-existing field. For normally magnetized shells (32.1) becomes

$$W = \tfrac{1}{2}\Sigma\iint\phi\frac{\partial\Omega}{\partial n}dS = -\tfrac{1}{2}\Sigma\phi n \quad . \quad . \quad . \quad (32.2)$$

n being the total number of tubes of induction crossing the shell.

If the energy is measured from a configuration in which the shells are complete but scattered at infinity—giving, that is, the work done in bringing together already constructed shells

$$W' = -\tfrac{1}{2}\Sigma\phi n' \quad . \quad . \quad . \quad . \quad . \quad (32.3)$$

where n' is not the total number of tubes actually crossing a shell, but the number which crosses it from the remaining shells.

For a system of current circuits

$$W = +\tfrac{1}{2}\Sigma\iota n \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

though a current circuit is equivalent to a magnetic shell for which $\phi = \iota$. The difference in sign arises from the fact that in addition to the external magnetic energy $+\frac{1}{2}\Sigma\phi n$, in the case of magnetic shells of finite thickness there is also a contribution due to the internal magnetic energy of amount $-\Sigma\phi n$.

Equation (32.1) gives the primary expression for the energy of a system of magnetized bodies. Writing $\mathbf{a} = \boldsymbol{\alpha} + 4\pi\mathbf{A}$, etc., and transforming by Green's Theorem, it may be shown that this is equivalent to

$$W = \frac{1}{8\pi}\iiint H^2 dv \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

the integration being taken throughout all space.

If, however, permanent and induced magnetism co-exist, $\mathbf{a} = \mu\boldsymbol{\alpha} + 4\pi\mathbf{A}$, and this leads to the more general expression

$$W = \frac{1}{8\pi}\iiint \mu H^2 dv \quad . \quad . \quad . \quad . \quad . \quad (34.1)$$

Thus magnetic energy may be regarded either as localized in the magnetized bodies, or as spread through the whole of space. Either standpoint leads to mathematical results, which, as far as they can be tested by experiment, are precisely the same.

Expressions for the forces can easily be calculated from those for the energy. (32.1) gives the energy of a magnetized body in a magnetic field $W = -\frac{1}{2}\iiint \mathbf{I}\cdot\mathbf{H}dv = -\frac{1}{2}\iiint \kappa H^2 dv.$

The force acting on it is given by

$$f = -\nabla W = +\tfrac{1}{2}\iiint \kappa\nabla H^2 dv = +\tfrac{1}{2}\iiint \kappa \operatorname{grad} H^2 dv \quad (35)$$

For a small isotropic body of volume v, susceptibility κ_1, suspended in a medium of susceptibility κ_2, this usually takes the special form, supposing the field gradient to be in the x direction,

$$f_x = (\kappa_1 - \kappa_2)v\mathrm{H}\frac{\partial \mathrm{H}}{\partial x} \quad . \quad . \quad . \quad . \quad (35{\cdot}1)$$

For the force acting across a boundary separating two media with its plane in the direction of the field

$$f = \frac{\mu_1 - \mu_2}{8\pi}\iint \mathrm{H}^2 d\mathrm{S} = \tfrac{1}{2}(\kappa_1 - \kappa_2)\mathrm{H}^2\mathrm{S} \quad . \quad . \quad (36)$$

The fact that a magnetized medium may be regarded as possessing magnetic energy of amount $\frac{\mu \mathrm{H}^2}{8\pi}$ per unit volume is equivalent to supposing that a system of tensions along the lines of force exists, and a pressure at right angles to them, together with a general "hydrostatic" pressure. All these are numerically equal to $\frac{\mu \mathrm{H}^2}{8\pi}$. When the pressure effect is considered, however, it must be remembered that any resulting change in volume may give rise to a change in μ, owing to the change in density τ, so that according to the statistical theory, in an isotropic medium, the force arising may be expressed in the form

$$f_x = \frac{\partial}{\partial x}\left(\frac{\mathrm{H}^2}{8\pi}\tau\frac{d\mu}{d\tau}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . (37)$$

If $\mu - 1 \propto \tau$, this may be written

$$f_x = \frac{\mu - 1}{8\pi}\frac{\partial \mathrm{H}^2}{\partial x} \quad . \quad . \quad . \quad . \quad . \quad . \quad (37{\cdot}1)$$

In such a medium, free to alter in volume, there will be magnetostrictive effects, equilibrium occurring when the pressure at each point is changed by amount $\frac{\mu - 1}{8\pi}\mathrm{H}^2$.

6. The Electron Theory

The inadequacy of statistical electromagnetic theory applied to the passage of light waves through material media, especially in connection with dispersion, made it clear that further advance necessitated some more detailed hypothesis as to the structure of matter. In this way the electron theory arose, attempts being made to interpret phenomena in terms of the properties of discrete electrical charges, positive and negative, out of which matter was assumed to be built up. The hypothesis was very general, and plausible, but it remained hypothesis until the actual discovery of the electron, of unique charge and mass. The elucidation of its properties was facilitated by the results of the previous hypotheses; now, however, the equations of electron theory may be stated simply as generalizations from experience. Statistical concepts (such as permeability and dielectric constant) drop out of the equations, which involve only the free space electric and magnetic vectors, the electric charges and their velocities. It becomes necessary later, as the work of synthetic theory, to interpret concepts applying to matter *en masse*, by a statistical treatment, in terms of the properties of the single electrons. The fundamental equations are

$$\nabla \cdot \mathbf{E} = 4\pi\varrho \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

$$\nabla \cdot \mathbf{H} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

$$\nabla \times \mathbf{E} = -\frac{1}{c}\dot{\mathbf{H}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

$$\nabla \times \mathbf{H} = \frac{1}{c}(\dot{\mathbf{E}} + 4\pi\varrho\mathbf{v}) \quad . \quad . \quad . \quad . \quad . \quad (41)$$

To these must be added the empirical expression for the force per unit charge acting on charges due to the electric and magnetic fields

$$\mathbf{F}\varrho = \mathbf{E}\varrho + \frac{1}{c}\mathbf{H} \times \mathbf{v}\varrho \quad . \quad . \quad . \quad . \quad . \quad (42)$$

For free space these assume the same form as those previously considered (4–7), while to (41) the discussion of equation (7.2) applies; $\frac{\varrho\mathbf{v}}{c}$ being substituted for **i**.

The second term on the right of (42) is a generalization of Ampère's rules for the force on current circuits in magnetic fields, the extrapolation to moving electrons being justified by the experiments on cathode rays. For ϱ, ne may be substituted, n being the excess of units of positive charge per unit volume, the unit being e, the electronic charge ($4{\cdot}774 \times 10^{-10}$ E.S.U.).

The solution of the equations—the determination of **E** and **H** at any point arising from any arbitrary motion of the charges —by direct attack presents formidable difficulties; but the problem is somewhat simplified by introducing, as auxiliary mathematical functions from which the electric and magnetic forces may be derived, the scalar and vector potentials ϕ and $\mathbf{A}$ such that

$$\mathbf{H} = \nabla \times \mathbf{A} \quad \dots \quad (43)$$

$$\mathbf{E} = -\frac{1}{c}\dot{\mathbf{A}} - \nabla\phi \quad \dots \quad (44)$$

The equations to be solved then assume the form

$$\left(\nabla^2\phi - \frac{1}{c^2}\frac{\partial^2\phi}{\partial t^2}\right) = -4\pi e \quad \dots \quad (45)$$

$$\left(\nabla^2\mathbf{A} - \frac{1}{c^2}\frac{\partial^2\mathbf{A}}{\partial t^2}\right) = -\frac{4\pi e\mathbf{v}}{c} \quad \dots \quad (46)$$

giving as solutions

$$\phi = \left[\frac{e}{\left(1 - \frac{v_r}{c}\right)}\right] \quad \dots \quad (47)$$

$$\mathbf{A} = \left[\frac{e\mathbf{v}}{rc\left(1 - \frac{v_r}{c}\right)}\right] \quad \dots \quad (48)$$

the square brackets indicating that the expressions within them are to be evaluated at the charge e not at time t, at which ϕ and $\mathbf{A}$ are being determined, but at the retarded time $t - \frac{r}{c}$, r being the distance of the point considered from the charge.

Let $$s = \left[r\left(1 - \frac{v_r}{c}\right)\right], \quad \kappa = \left[\left(1 - \frac{v_r}{c}\right)\right]$$

From (4) and (48), using (43) and (44), the following explicit expressions for $\mathbf{E}$ and $\mathbf{H}$ may be derived:

$$\mathbf{E} = -\frac{e\dot{\mathbf{v}}}{c^2\kappa s} + \frac{e}{\kappa s^2}\left(\mathbf{r}_1 - \frac{\mathbf{v}}{c}\right)\left(1 + \frac{\mathbf{r}\cdot\dot{\mathbf{v}}}{c^2} - \frac{\mathbf{v}^2}{c^2}\right) \quad \cdot \quad (49)$$

$$\mathbf{H} = \mathbf{r}_1 \times \mathbf{E} \quad \dots \quad (50)$$

Thus $\mathbf{H}$ and $\mathbf{E}$ are mutually at right angles, and in magnitude equal to each other. The content of the equations may be realized most easily by considering a few special cases, and assuming $\frac{v}{c}$ to be small.

For r small

$$\mathbf{E} = \frac{e}{r^2}\mathbf{r}_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (51)$$

$$\mathbf{H} = \frac{e}{cr^2}\mathbf{r}_1 \times \mathbf{v} \quad . \quad . \quad . \quad . \quad . \quad . \quad (52)$$

For r large

$$\mathbf{E} = -\frac{e}{c^2 r}\dot{\mathbf{v}}_n \quad . \quad . \quad . \quad . \quad . \quad . \quad (53)$$

$$\mathbf{H} = -\frac{e}{c^2 r}\mathbf{r}_1 \times \dot{\mathbf{v}}_n \quad . \quad . \quad . \quad . \quad . \quad (54)$$

From (53) and (54) the energy radiated from an electron may be calculated; by Poynting's Theorem the flux of energy across a surface is given by $\mathbf{\Pi} = \frac{c}{4\pi}\mathbf{E} \times \mathbf{H}$, and hence for the total flux of energy from an electron per unit time

$$-\frac{d\mathrm{W}}{dt} = \iint_{\mathrm{S}} \Pi d\mathrm{S} = \frac{2}{3}\frac{e^2\dot{v}^2}{c^3} \quad . \quad . \quad . \quad (55)$$

For an electron describing an orbit with an angular velocity ω, radius d, this gives

$$-\frac{d\mathrm{W}}{dt} = \frac{2}{3}\frac{e^2}{c^3}d^2\omega^4 \quad . \quad . \quad . \quad . \quad . \quad . \quad (55{\cdot}1)$$

It is here that one of the main stumbling-blocks of classical electromagnetic theory is encountered. Atoms are built up of a comparatively massive positively charged nucleus, with electrons surrounding it. For equilibrium, it is necessary to assume that the electrons are moving in orbits with appropriate velocities. According to (55·1) they would be continually losing energy by radiation. Without constantly supplied work the electron would eventually come to rest, falling into the nucleus. The world would consist of conglomerates of positive and negative charges. Atoms, however, are essentially stable structures. The electrons definitely are not continually losing energy by radiation. The quantum theory evades the difficulty by taking as a fundamental postulate that there are certain possible "stationary" states in which the electrons do not radiate; but the difficulty remains. That radiation should occur seems an unavoidable consequence of the fundamental electron theory equations, which themselves are direct generalizations from experience; and yet it seems equally an experimental fact that accelerated motion of electrons is not necessarily associated with radiation. The escape from this dilemma has not yet been found. The consequences of the electron theory may give the truth, but they do not give the whole truth; the fact that radiation does not occur under certain circumstances is not explained by an arbitrary postulate; there must be some natural, but hitherto unrecognized, restriction to the range of validity of the results deduced from classical theory.

It may be mentioned that while accelerated motion is not always associated with radiation, radiation is invariably associated with change of energy of the electrical "radiating" system. The energy change is more fundamental than acceleration, and it may be suggested that even if there is acceleration, there will be no radiation unless the acceleration corresponds to an energy change. The equations (38)–(41) only enable the electric and magnetic fields to be calculated which arise from an arbitrary motion impressed on the charges; and while for an isolated charge the energy change involved in acceleration could only be compensated by radiational effects, radiation may not necessarily occur when the motions of the charges are controlled by the mutual action of all the members of a system of which they form part.

7. Magnetic Properties of Orbital Electrons

From the point of view of magnetic theory the properties of electrons moving in orbits possess particular importance, for it is clear, bearing in mind the relation between moving charges and electric currents, that such orbital electrons will behave to a certain extent as small magnets, constituting, in fact, physical magnetic "elements." The difficulties in connection with radiation, however, led to the invention of hypothetical magnetons, consisting of swirls of continuous electricity in the form of rings or spheres which might be supposed to give rise to magnetic fields but not to radiation. There is no experimental evidence for the existence of such magnetons; and as the radiation dilemma applies to electrons in general, the properties of these hypothetical magnetons are of little physical interest; magnetic phenomena must be explained on the basis of the experimental electron.

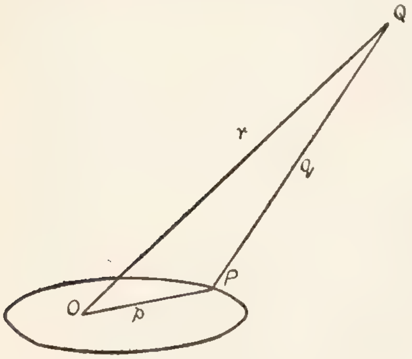

FIG. 2.

In considering the purely magnetic properties of orbital electrons it will be legitimate, in approximate treatment, to omit the dubious radiation terms, and also only to consider those remaining terms of greatest importance (omitting, that is, the higher powers of $\frac{v}{c}$).

Let O be the focus of the electron orbit, **p** the radius vector, **q** the distance of the electron from the point Q considered, and **r** the distance OQ.

$$\mathbf{q} = \mathbf{r} - \mathbf{p}$$

$$\frac{1}{q} \doteq \frac{1}{r}\left(1 + \frac{\mathbf{r}\cdot\mathbf{p}}{r^2}\right)$$

and for the vector potential, from (48), as an approximate expression

$$\mathbf{A} = \frac{e}{cr}\mathbf{v}\left(1 + \frac{\mathbf{r}\cdot\mathbf{p}}{r^2}\right) \quad . \quad . \quad . \quad . \quad . \quad (56)$$

The mean value of **A** as the electron describes its orbit is required, that is $\frac{1}{t}\int_t \mathbf{A}dt$.

Now $\dot{\mathbf{p}} = \mathbf{v}$; and, since $\mathbf{r} \times \dot{\mathbf{p}} \times \mathbf{p} = \dot{\mathbf{p}}(\mathbf{r}\cdot\mathbf{p}) - \mathbf{p}(\mathbf{r}\cdot\dot{\mathbf{p}})$ and $\frac{\partial}{\partial t}\mathbf{p}(\mathbf{r}\cdot\mathbf{p}) = \dot{\mathbf{p}}(\mathbf{r}\cdot\mathbf{p}) + \mathbf{p}(\mathbf{r}\cdot\dot{\mathbf{p}})$, $\mathbf{v}(\mathbf{r}\cdot\mathbf{p}) = \frac{1}{2}\frac{\partial}{\partial t}\mathbf{p}(\mathbf{r}\cdot\mathbf{p}) + \frac{1}{2}(\mathbf{r} \times \dot{\mathbf{p}} \times \mathbf{p})$

$$\mathbf{A} = \frac{e}{cr}\left[\frac{\partial}{\partial t}\mathbf{p} + \frac{1}{2r^2}\frac{\partial}{\partial t}\mathbf{p}(\mathbf{r}\cdot\mathbf{p}) + \frac{1}{2r^2}(\mathbf{r} \times \dot{\mathbf{p}} \times \mathbf{p})\right] \quad . \quad (57)$$

In calculating the mean value of **A**, the first two terms, being complete differentials, will have no effect, hence

$$\bar{\mathbf{A}} = \frac{e}{2cr^3}(\mathbf{r} \times \dot{\mathbf{p}} \times \mathbf{p}) \quad . \quad . \quad . \quad . \quad . \quad (58)$$

Comparing this with (30) it will be seen that as far as mean magnetic effect is concerned an electron moving in an orbit is equivalent to a magnet of moment

$$\boldsymbol{\mu} = \frac{e}{2c}\mathbf{p} \times \dot{\mathbf{p}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (59)$$

Now $\frac{1}{2}\mathbf{p} \times \dot{\mathbf{p}}$ is the rate of description of area, and for ordinary orbital motions is constant. Let S be the area of the orbit, τ the periodic time, $\mathbf{n}_1$ the unit normal to the orbital plane.

The expression for $\boldsymbol{\mu}$ may be put in the following equivalent forms

$$\boldsymbol{\mu} = \frac{e}{2c}\mathbf{p} \times \dot{\mathbf{p}} = \frac{eS}{c\tau}\mathbf{n}_1 \quad . \quad . \quad . \quad . \quad . \quad (59{\cdot}1)$$

Writing $\mathbf{j}$ for the angular momentum, since $\mathbf{j} = m\mathbf{p} \times \dot{\mathbf{p}}$

$$\boldsymbol{\mu} = \frac{e}{2mc}\mathbf{j} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (60)$$

Here it should be noticed that $\mathbf{j}$ is the angular momentum of the orbital electron itself about the centre towards which its acceleration is directed; not the momentum of the system as a whole of which it forms part.

Electrons rotating in orbits, then, possess the properties of magnets, and may be taken as forming the physical magnetic elements; the magnetic properties of matter *en masse* must be explained in terms of their reaction to external fields applied; further theoretical developments will be given in due course; the present chapter has been concerned with such fundamental consequences and results of the classical theory, as must form the basis of any subsequent treatment.

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The first chapter contains a wonderfully clear and beautiful account of the general principles of the theory of electrons. (6)

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CHAPTER III

EXPERIMENTAL METHODS AND SURVEY OF EARLIER RESULTS

1. General Account of Methods for Determining Susceptibilities

THE methods for investigating the magnetic properties of strongly magnetic substances such as iron, nickel and cobalt are of fundamental importance, since by means of them the main characteristics of magnetic phenomena, which form the basis of classical theory, were worked out. The phenomena of hysteresis and residual magnetism, moreover, which occur with ferromagnetics, while as yet incompletely understood, will undoubtedly throw much light on the general problem of magnetism. The effects with ferromagnetics being large, there are no great experimental difficulties involved in studying their main features. The magnetometric and ballistic methods which are used are well known, detailed descriptions of them being given in practically all standard textbooks, so they will not be discussed here. Outside ferromagnetic metals and alloys, the range of substances for which what may be termed " ferromagnetic methods " may be successfully employed is very limited ; but brief mention may be made of their application to strongly paramagnetic solutions by Townsend (1896) and to bismuth, which is strongly diamagnetic, by von Ettingshausen (1882) and others. Essentially the method involves the measurement of the change in induction through a coil when the substance under investigation is substituted for air as the core.

In von Ettingshausen's experiments two primary coils in series had secondaries wound round them which were connected in opposition through a galvanometer. Using an interrupted current in the primary circuit, with a synchronous commutator in the secondary, a balance was obtained ; a bismuth cylinder was then inserted in one of the primary coils, and the disturbance of the balance was compared with that produced by substituting for the bismuth a solenoid through which a known interrupted current was passed. From the results the permeability of bismuth could be calculated. Care must be taken that the frequency of interruption of the currents is not so great that the Foucault currents induced in the bismuth at make and break produce a resultant effect on the galvanometer. Townsend's method was similar. One of the primary coils consisted of a solenoid of length l, with N turns surrounding a jar of cross-sectional area A. Round the middle was a secondary of N′ turns. On filling the jar with a solution of susceptibility κ, the effect due to the increase in the mutual induction between the two coils, equal to $4\pi\kappa . \frac{4\pi NN'A}{2l}$, was balanced with the aid of a variable mutual inductance.

The change in induction produced by most substances is small and difficult to measure accurately. Theoretically, however, it is possible to measure a very small change in an inductance using a heterodyne beat method with two almost synchronous oscillating valve circuits. The frequency of oscillations is given approximately by $\frac{1}{2\pi\sqrt{LC}}$; if two circuits are first in tune, and the frequency of one of them is altered by changing the inductance in it, beats will be obtained, the number of beats being given by

$$n = \frac{1}{2\pi\sqrt{C}}\left[L^{-\frac{1}{2}} - L_1^{-\frac{1}{2}}\right]$$

$$= \frac{1}{2\pi\sqrt{LC}}\left[1 - \left(\frac{L}{L_1}\right)^{\frac{1}{2}}\right]$$

$$= \tfrac{1}{2}N\frac{\delta L}{L} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Theoretically, since N may be made large, very small changes in L may be measured, and hence, if these are brought about by the insertion of magnetic substances in a solenoid, small susceptibilities may be accurately determined. The method has been used by Belz and Wagstaff. The numerous experimental difficulties in connection with subsidiary sources of disturbance, however, render the method less promising than it at first sight appears.

The methods most generally useful for substances of low susceptibility are those of Faraday, based on the measurement of the force on a small specimen in a non-homogeneous field, and of Gouy, in which a cylinder is suspended so that one end is in a homogeneous field, the other in a region where the field is negligible; with the extension to liquids in Quincke's capillary ascension method. A number of dynamical methods are also available. The essential features of these will now be described, the experimental details and elaborations being reserved for consideration in connection with particular researches.

Faraday Method.—The force acting on a substance of permeability μ_1, suspended in a medium of permeability μ_2, is given by (cf. II, 35)

$$F = \frac{\mu_1 - \mu_2}{8\pi} \int \nabla H^2 dv \quad . \quad . \quad . \quad . \qquad (2)$$

Now $\mu = 1 + 4\pi\kappa$; if the body is small (volume v), so that the field is uniform over it, and if the field is in the y, and its gradient in the x direction, this becomes

$$F_x = (\kappa_1 - \kappa_2) v H_y \frac{\partial H_y}{\partial x} \quad . \quad . \quad . \quad . \quad . \qquad (2.1)$$

A suitable non-homogeneous field with an axis of symmetry may be obtained by inclining two pole pieces of an electromagnet to each other. The force on a specimen investigated may be measured by supporting it, in the form of a small rod, from one end of a torsion arm; the constants of the suspending fibre or wire are determined; and the force is estimated directly from the displacement, if this is small, or by observing the twist of the torsion head required to bring back the specimen to the zero position. For absolute determinations the weaknesses of the method are obvious. H and $\frac{\partial H}{\partial x}$ at the specimen have to be found. In general the integration in (2) could only be carried out approximately and the assumptions involved in (2.1) are seldom completely justified. Even if they were, however, it is very difficult to be sure that the field is determined, usually by a search coil and ballistic galvanometer, at exactly the region occupied by the specimen; and that the field and its gradient are being determined for the same points.

For relative measurements, however, the Faraday method is one of the most convenient; the main difficulties arising in connection with the constancy and reproducibility of the fields, and the setting of the specimens. It has been extensively used, in particular by Curie (sect. 4), so that it sometimes goes by his name.

The susceptibility of liquids and gases may be found by placing them in suitable vessels, carrying out blank experiments; or, sometimes more conveniently, by using them as the "surrounding medium."

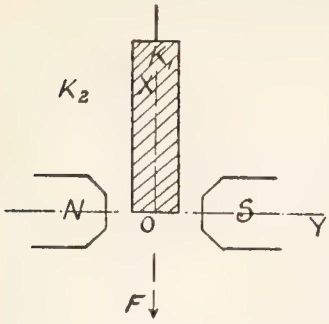


FIG. 3.—Gouy Method for Susceptibilities.

Gouy Method.—In this method a uniform cylinder or prism of cross-sectional area A is suspended with one end in a homogeneous field between the poles of a magnet (the axis of the cylinder being at right angles to the field), the other end in a region where the field is negligible.

The force acting on the cylinder along its axis is then given by

$$F = \frac{\mu_1 - \mu_2}{8\pi} H^2 A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$F = \tfrac{1}{2}(\kappa_1 - \kappa_2) H^2 A \quad . \quad . \quad . \quad . \quad . \quad . \quad (3{\cdot}1)$$

(This may be derived by considering the lateral pressure in the "tubes of force"; or the force acting on each element of volume as in (2) above, giving $F = \tfrac{1}{2}\kappa \int_0^l \frac{\partial H^2}{\partial x} A\,dx = \tfrac{1}{2}\kappa A H^2$; or most simply, the change in energy resulting on a small displacement.)

If the field is not negligible at the other end of the cylinder (3·1) becomes

$$F = \tfrac{1}{2}(\kappa_1 - \kappa_2) A (H_1^2 - H_2^2) \quad . \quad . \quad . \quad (3{\cdot}2)$$

The force may be determined by direct weighing, using a sensitive balance of special type; or the cylinder may be supported horizontally from a torsion arm. For absolute measurements H has to be determined, but this is comparatively simple, as there may be a relatively large region in which the field is uniform; a search coil may be used, but a frequently more convenient method is to measure the force exerted on a current-bearing wire, this being substituted in place of the cylinder. The method is suitable for solids, liquids or gases, and is probably the most generally applicable for absolute measurements, though somewhat less convenient than the non-homogeneous field method for relative determinations.

Quincke's Capillary Ascension Method for Liquids.—This is based on the same principle as Gouy's method. Essentially a U-tube is employed, one limb being of wide, the other of narrow bore.

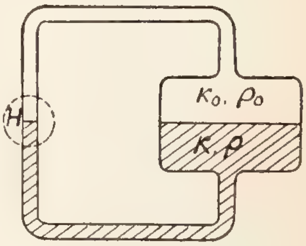


FIG. 4.—Quincke Method for Liquids and Gases.

The narrow tube passes between the poles of a magnet, the meniscus being in a region where the field is uniform; and the apparatus is so arranged that the field at the liquid surface in the wide tube is negligibly small. When the field is applied the meniscus will rise or fall by an amount δ such that

$$p = \delta\varrho g = \tfrac{1}{2}(\kappa - \kappa_0)H^2 \quad . \quad . \quad . \quad . \qquad (4)$$

κ being the susceptibility of the liquid, ϱ its density, and κ_0 the susceptibility of the gas.

$$\frac{\kappa}{\varrho} - \frac{\kappa_0}{\varrho_0} = \frac{2\delta}{gH^2}$$

$$\chi = \frac{2\delta}{gH^2} + \frac{\varrho_0}{\varrho}\chi_0 \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4.1)$$

If the displacement is observed the bore must be uniform.

The usual precautions against sticking must be taken, as in surface-tension experiments. One of the great advantages of the method is that the presence of dust particles, even of substances of high susceptibility, does not affect the results; and no blank experiments have to be carried out to allow for the magnetic properties of the glass container.

The magnitude of the displacement may be illustrated by the fact that for water, with a field of 20,000 gauss, $\delta = 1{\cdot}46$ mm. For solutions of paramagnetic salts (as of Fe, Mn) the effect may be as much as 100 times greater.

The method may be modified by adding liquid to or removing it from that in the wide limb, so as to maintain the meniscus constant in position. The pressure change can then be estimated from the volume of liquid added or removed, and the cross-sections of the two limbs of the U-tube.

Dynamical Methods.—If suspended between the poles of a magnet, a magnetic substance will tend to take up an equilibrium position.

An elongated specimen, if diamagnetic, will in general set itself equatorially (along OX); if paramagnetic, axially (along OY). If displaced from the equilibrium position, oscillations will occur, and these, if the amplitude is small, will be simple harmonic, and of period independent of the form of the specimen, and depending only on its susceptibility, and on the magnetic field.

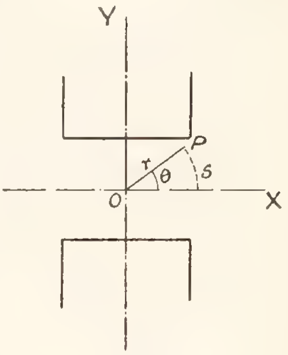


FIG. 5.

Suppose the field is symmetrical about OX and OY. Then at any point not too far from O (Fig. 5)

$$H^2 = H_0^2 - ax^2 + by^2$$

Consider an element δv of the substance at P. For the force along s

$$F_s = \tfrac{1}{2}\kappa\delta v\frac{\partial H^2}{\partial s} = \tfrac{1}{2}\kappa\frac{\delta v}{r}\frac{\partial H^2}{\partial \theta}$$

$$H^2 = H_0^2 - ar^2\cos^2\theta + br^2\sin^2\theta$$

$$\frac{\partial H^2}{\partial \theta} \doteqdot 2r^2(a + b)\theta \text{ for } \theta \text{ small}$$

$$F_s = \tfrac{1}{2}\frac{\kappa\delta v}{r}2r^2(a + b)\frac{s}{r} = \kappa\delta v(a + b)s$$

$$\ddot{s} = \kappa\frac{\delta v}{\delta m}(a + b)s = \chi(a + b)s$$

This is independent of r, so that a specimen of arbitrary form will execute harmonic oscillations.

If T is the period, for a diamagnetic

$$\chi = -\frac{4\pi^2}{T^2(a + b)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Similarly, for a paramagnetic, remembering that θ is measured from OY,

$$\chi = +\frac{4\pi^2}{T^2(a + b)}$$

The first absolute measurements were made by Rowland by a method based on these principles ; a very careful investigation of the field is necessary and it is obvious that a number of elaborate corrections would have to be made if results of high accuracy were required.

A method suggested by Sève is of interest, though it does not seem to have been applied practically. Consider a pendulum vibrating so that at one end of its swing (amplitude α) the bob is in a magnetic field, and at the other end (amplitude β) in a region where the field is negligible. The energy is wholly potential in each position, being partly magnetic (of amount W) when the bob is in the field, so that

$$W + \tfrac{1}{2}C\alpha^2 = \tfrac{1}{2}C\beta^2$$

$$\tfrac{1}{2}\kappa H^2 v = \tfrac{1}{2}C(\beta^2 - \alpha^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The susceptibility could thus be determined from observations on the amplitude of the swings.

2. The Production and Measurement of Magnetic Fields

The production of magnetic fields of the order of a few thousand gauss presents no particular difficulty; but in investigating the magnetic properties of substances of low susceptibility, and the Zeeman effect, much stronger fields are desirable. The field between the poles of an electromagnet when these are plane and circular of radius r, and distance $2a$ apart, is given by

$$H = 4\pi I\left(1 - \frac{a}{\sqrt{a^2 + r^2}}\right) \quad . \quad . \quad . \quad . \quad . \quad (7)$$

having a limiting value of

$$H = 4\pi I \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.1)$$

I being the intensity of magnetization.

If L is the effective length of the magnetic circuit, S the cross-section of the material of the magnet, and l and s the length and cross-section of the interspace between the poles, N the number of turns of the winding, and i the current,

$$\frac{4\pi Ni}{10} = \frac{LHs}{\mu S} + Hl = H\left(\frac{Ls}{\mu S} + l\right) \quad . \quad . \quad . \quad . \quad (8)$$

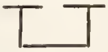
As shown by (7) the field obtainable is limited by the saturation intensity of magnetization; for this reason ferro-cobalt is often substituted for iron for the pole pieces, the saturation intensity being some 10 per cent. greater. From (8) it is clear that for a given number of ampere turns, the field will be greater the smaller the interspace; and the greater the cross-section of the iron of the magnet. High fields therefore necessitate the use of massive electromagnets, the cross-section of the iron often being about 150 square centimetres. The cross-section of the interspace, however, should be small. Conical pole pieces were introduced by Ewing, and, as a result of his work and that of Weiss and others, are now extensively employed. The maximum field is obtained for a semi-angle of the cones of $54° 44'$ (though for maximum homogeneity the angle is $39° 14'$).

With the optimum angle for strong fields

$$H = 4\pi I\left(1 + \frac{2}{3\sqrt{3}}\log\frac{r}{a\sqrt{2}} - \frac{1}{\sqrt{3}}\right) \quad . \quad . \quad . \quad (9)$$

$$= 4\pi I\left(0{\cdot}2893 + {\cdot}8863\log\frac{r}{a}\right) \quad . \quad . \quad . \quad . \quad (9.1)$$

Thus if the pole-face diameter $(2r)$ is large compared with the interspace distance ($2a$), fields considerably in excess of those calculated from (7.1) may be obtained; for $\frac{r}{a} = 20$, for example $H = 1{\cdot}442 \times 4\mu I$.

Electromagnets are now usually made in the half-ring or rectangular  shape due respectively to Boas and Weiss. The Weiss form is generally the most convenient in that the inter-pole distance can be easily adjusted. The conical pole pieces are of ferro-cobalt. Patterns are available with mechanical devices for adjustment of height and orientation of the whole magnet. To ensure constancy and reproducibility of the field, it is necessary that the windings and the magnet should be maintained at constant temperature. This is brought about by having tubular windings, through which a stream of water passes.

With a typical Weiss electromagnet the field in an interspace $3\frac{1}{2}$ mm. long between pole faces 6 mm. in diameter, varied from 7,200 gauss, for 5,000 ampere turns, to 31,100 gauss, for 50,000 ampere turns. Magnetic saturation limits the maximum fields obtainable by iron-cored magnets over a volume of a few cubic millimetres to something of the order of 50,000 gauss.

The methods for measuring magnetic fields are well known, and need only be briefly referred to. The most generally useful is the induction method in which the change in the magnetic flux through a small coil of many turns due to turning it through 180° or reversing the field is measured by means of a ballistic galvanometer or fluxmeter. The force on a current-bearing conductor may be measured directly, but this method is not usually suitable for measuring fields which are only constant over a small region; but it is sometimes applied in connection with the Gouy method for susceptibilities, as in Wills' experiments (sect. 3). The change in the specific resistance of a bismuth wire in a magnetic field provides a means of measuring fields which are constant over only small regions or for making "topographic" surveys. The wire must, however, be calibrated; and the method is unsuitable for fields which are varying, owing to hysteresis effects. The Quincke method for liquid susceptibilities may, of course, be applied inversely to the measurement of fields, using a liquid of known susceptibility. An apparatus based on this has been elaborated by du Bois in which the sensitivity is increased by having the narrow tube inclined at a suitable angle θ when (cf. 4)

$$H = \sqrt{\frac{2g\varrho}{\kappa}}\sqrt{\Delta\,\delta\sin\theta} \quad . \quad . \quad . \quad (10)$$

Somewhat analogously, in studying the Zeeman effect, the field may be estimated from the separation of the components of a line whose behaviour in absolutely measured fields has been determined.

The present is a convenient place for giving a short outline of a method which has recently been used by Kapitza, at the Magnetic Department of the Cavendish Laboratory at Cambridge, for producing very intense fields. As already pointed out, the use of an iron core in solenoids diminishes the "magnetic resistance," but the fields obtainable are limited by the saturation of the iron. The production of large fields with uncored solenoids is limited by the very powerful sources of electrical energy required, and the necessity of avoiding overheating of the coil. Liquid air is efficient as a cooling agent, and also decreases the resistance of the coil, and so the power required; but Fabry showed that to produce a field of 100 kilogauss in a coil of one centimetre internal diameter, with a source of 100 kw., some 24 litres of liquid air per minute would be necessary for cooling.

The essential feature of Kapitza's method is to eliminate the overheating by producing the fields only for a very short time (some hundredth of a second) which is nevertheless long enough for atomic magnetic effects to develop normally. Simple in idea, in application very considerable technical and experimental difficulties have to be overcome.

The power necessary varies as the square of the field required. Powers of 1,200 kw., used in Kapitza's experiments, would be obtainable by means of a large and costly electro-generator plant, but when the energy is only required for a short time, any form of apparatus may be employed which is capable of storing energy over a long period and liberating it in a short one. To store quantities of energy of the order of 2·5 great calories, using condenser batteries, a large capacity (50 mf.) would be necessary, and high tensions (50 kv.) would have to be employed. The practicability of utilizing energy magnetically stored in a large iron core, magnetized by a current through a primary, was investigated; if this energy could be transferred to a secondary of few turns and low resistance by suddenly breaking the primary current, large secondary currents would be obtained; but it was found that energy transfer was diminished owing to the primary spark at break. A method being investigated is the mechanical storage of energy in a fly-wheel connected to a generator; this energy being liberated with considerable power increase by suddenly switching in a small resistance.

Actually a chemical method was adopted, the energy being stored by means of accumulator batteries of a specially constructed type; these consisted of 1·5 mm. lead plates (70 in each battery) of large area (35×35 cm.), separated by rubber discs and edging at a small distance apart (1·5 mm.), each gap being filled by 30 per cent. sulphuric acid; the resistance of the whole battery was thus small (·02 ohm). A set of four such batteries was used. The batteries were charged at 220 volts, 2–3 amperes. On discharging through a resistance of ·02 ohm, 1,000 kw. was obtained, corresponding to a power increase coefficient greater than 2,000.

In the most efficient discharge (through ·025 ohm) the current was 7,000 amperes, while short-circuiting produced a current of 14,000 amperes! The current fell off with time, and to avoid overheating of the coils, could be broken by a special short-circuit switch consisting essentially of a copper-wire fuse.

The main difficulties in the use of the batteries arose from bursting of the lead plates, probably due to the active deposit breaking off in places and connecting with the opposite plate; sulphation, unequally distributed, will occur, and on discharge very high currents may pass in a few places resulting in fusion.

An elaborate switch-gear was necessary for making and breaking the currents; not only on account of the magnitude of the currents, but also because the make and break had to occur at definite adjustable time intervals. It was arranged that the release of a photographic plate automatically set in train the whole series of operations; on this plate were recorded the currents and tensions by means of high-frequency oscillographs introduced as shunts.

As to the coils used for the production of the magnetic fields, it has been shown by Fabry that the shape is of little importance, the field at the centre of the coil being given by

$$H = k\sqrt{\frac{W}{\varrho\eta a}} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where W is the power of the source of electrical energy, a the radius of the opening, ϱ the specific resistance of the coil material, and η the coefficient of filling (the ratio of the total cross-section of the winding to the section filled by the conductor); k is usually between ·15 and ·27. In these experiments the question of self-induction also enters; for a coil with many turns, and high self-inductance, the current may only attain its maximum value when the accumulator energy is nearly exhausted. Coils were made, guided by theoretical considerations, and the most suitable found by trial. To make η as near unity as possible, flat coils were used, windings being of copper band insulated by shellac-soaked silk ribbon. The coils were used in pairs, a typical coil having 48 turns, internal and external radii 1·2 and 2·7 cm., and a height (width of copper band) 1·6 cm.

The constants of the double coil were found experimentally by suspending a small magnetic needle at the centre of the coil; and suspending this in turn at the centre of a large standard coil, so that planes and centres coincided. The constants of the large coil could be accurately calculated; the constants of the small coil could be found from the ratio of the currents passing through the two coils in opposite directions, which produced zero resultant effect on the needle.

The magnitude of the fields developed could then be determined from the currents. With the coil specified above fields of 75–80 kilogauss were obtained; with a coil of 1 mm. internal diameter, 500 kg. for 3/1000 second. It is interesting to note that in these experiments the current densities were of the order of 100,000 amps. per sq. cm. Kapitza estimates that it would be quite possible by an extension of these methods to produce in a coil of 1 mm. internal diameter fields of 2–3 million gauss, or even greater if liquid-air cooling could be made use of.

So far fields produced in this way have been applied to the study of α-particles, using a small Wilson cloud chamber and investigating the curvature of the tracks; and of the Zeeman splitting of spectral lines, particularly in connection with the Paschen-Back effect. There are still many technical difficulties to be overcome; but the method will undoubtedly have far-reaching applications, which cannot fail to throw light on many fundamental problems of atomic structure.

3. Some Early Investigations

Soon after his discovery of the "universality" of magnetism and his differentiation of substances of low susceptibility into dia- and para-magnetics, Faraday made a large number of comparative measurements, using the method which goes by his name.

A large permanent horse-shoe magnet was employed, the cylindrical-shaped specimens (S) being suspended at about half an inch from the strongest part of the field by a glass fibre connected to a torsion rod, which was parallel to AB (Fig. 6).

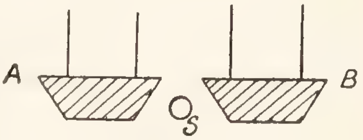


Fig. 6.—Faraday Arrangement.

The rod was supported by a fibre attached to a graduated head. The force on the specimen was measured by the turn of the head necessary to restore the torsion rod to its zero position.

As standard force of 100 was taken that on water in air, calculated from the torsion head readings corresponding to a cylinder of glass suspended first in air, and then in water.

$$\kappa_G - \kappa_A = k\theta_A \quad \kappa_G - \kappa_W = k\theta_W$$

so that

$$\kappa_W - \kappa_A = k(\theta_A - \theta_W) = 100.$$

The susceptibility of any liquid could then be determined on this scale by suspending the cylinder in it, and finding the corresponding restoring torsion.

$$\kappa_G - \kappa_L = k\theta_L$$

$$\kappa_L - \kappa_A = k(\theta_A - \theta_L) = 100\frac{\theta_A - \theta_L}{\theta_A - \theta_W} \quad . \quad . \quad (12)$$

For solids, cylinders of the same shape and size as the glass were used; and a bulb was also employed which could be filled with different liquids or gases, or evacuated; so that values for susceptibilities of substances in vacuo could be deduced. It is perhaps of interest to quote a few of Faraday's relative values.

Oxygen . .	+ 17·5
Air . .	+ 3·4
Hydrogen . .	− 0·1
Zinc . .	− 74·6
Water . .	− 96·6
Sulphur . .	− 118
Bismuth . .	− 1967

TABLE I.—VOLUME SUSCEPTIBILITIES (FARADAY) RELATIVE TO WATER IN AIR = 100.

Somewhat similar experiments were carried out by Plücker (1849) and Becquerel (1851).

Apparently the earliest absolute determinations were made by Rowland and Jacques, who used the vibrating-needle method. They found that the susceptibility of crystals might vary for different axes, values obtained for bismuth along two axes being $\kappa = -12{\cdot}55 \times 10^{-6}$ and $\kappa = -14{\cdot}32 \times 10^{-6}$ and for calc-spar $-{\cdot}038 \times 10^{-6}$ and $-{\cdot}040 \times 10^{-6}$.

Von Ettingshausen did some useful work in checking experimentally the equivalence of various methods for measuring susceptibility, bismuth being investigated in four different ways (1882). The first of these has already been described (sect. 1). The second was virtually the Gouy cylinder method, while the third was a modification of that of Rowland and Jacques. In the fourth method the bismuth was placed between the poles of a strong magnet, where it behaved as a weak reversed magnet. Its effect on a previously compensated magnetometer needle —the direct effect producing a deflection $\theta = \frac{2M}{Hd^3}$ would be very small—was found by observing the amplitude of swing attained by the needle when the bismuth was inserted and withdrawn with a periodicity equal to that of the needle. The results for the susceptibility by the different methods were $10^{-6}\kappa = 13{\cdot}57$, $14{\cdot}11$, $15{\cdot}3$ and $13{\cdot}6$. The Gouy method was considered most accurate.

It will be convenient here to refer briefly to a few experiments in which special points were investigated, although they are of slightly later date than Curie's work, which will be considered in the next section.

Wills (1896) studied a number of substances by the Gouy method, the specimens being in the form of rectangular plates, which were suspended from one arm of a balance so that the lower edge was horizontal and between the poles of an electromagnet. The field was neatly determined, with the same arrangement of apparatus, from the vertical force experienced by a "dummy" plate of the same shape as the specimens, when a known current was passed through a tin-foil strip passing round its two vertical and lower horizontal edges. For Bi, Sb and Al the values found for $10^6\kappa$ were $-12{\cdot}25$ to $-12{\cdot}55$, $-0{\cdot}714$ and $+1{\cdot}88$. With Bi, with fields varying from 1,600 to 10,000 gauss, the important result emerged that its diamagnetic susceptibility was independent of field strength, the behaviour thus contrasting with that of ferromagnetics.

A number of solutions of salts containing iron were examined by Townsend (1896) by the solenoid method. Allowing for the diamagnetism of the water (for which Townsend obtained $10^6\kappa = -{\cdot}77$) it was found that ferrous and ferric salts were paramagnetic, the susceptibility being proportional to the mass of iron in solution, and independent of the nature of the acid radicle. If m is the number of grams per c.c. of iron in solution, for the susceptibilities of the dissolved salts (found to be approximately the same as those for the dry salts) the values found were

Ferric Salts.	Fe_2Cl_6, $Fe_2(SO_4)_3$, $Fe_2(NO_3)_6$	$10^6\kappa = 266$ m.
Ferrous Salts.	$FeCl_2$, $FeSO_4$	$10^6\kappa = 206$ m.

When the iron was in the acid radicle, however, as in ferro- and ferri-cyanides, the magnetic effect was at least 100 times less. (It is worthy of note in this connection that iron carbonyl $Fe(CO)_5$ is diamagnetic.) Townsend's seem to have been the first considerable investigations in a field of magnetism which has yielded results of the utmost importance from an atomic standpoint (Chs. VI and VII).

In 1891 Dewar found that the paramagnetic properties of oxygen were greatly enhanced when it was liquefied; and a few years later he and Fleming measured its susceptibility by weighing balls of various substances suspended in a non-homogeneous field first with air and then with liquid oxygen as the surrounding medium. This gave a mean result, at – 182° C., of $10^6\kappa = +324$.

From the experiments previous to those of Curie, a few of which have been described, no very general conclusions could be drawn. The susceptibilities varied from substance to substance in an erratic manner, and seemed to have little relation to other properties; little was known about their variation with temperature; no definite decision could be made as to whether ferro-, para- and dia-magnetism were fundamentally distinct or not; and if there was such a thing as "atomic susceptibility" it apparently varied with the mode of combination of the atom. All the observations had, in a sense, been isolated. A comprehensive experimental survey of a wide range of substances under widely varied conditions was needed before much further progress could be made in elucidating the significance of magnetic phenomena.

4. The Work of Curie

Curie's work on the *Magnetic Properties of Bodies at Different Temperatures* (1895) is worthy to take rank among the great classical experimental researches, and will be described in some detail. Previous results were co-ordinated and an extensive series of new measurements were made. The whole investigation may be said to form the experimental foundation for modern theoretical work on magnetism; and the general survey of the wide field made clear which were the points which called for further, or more specialized, experimental investigation.

Curie wished to determine whether dia-, para- and ferromagnetism were fundamentally distinct; primarily by studying the effect of varying temperatures on the susceptibilities of substances of different types. The previous observations were insufficient to enable any generalizations to be made; for a number of paramagnetics, Wiedemann and Plessner had found a linear variation of $\frac{1}{\chi}$ with T; among diamagnetics Plücker had found that χ decreased with T for Bi, and remained constant for S and Hg; while Rowland, Hopkinson, and others had investigated ferromagnetics, and the practically complete disappearance of ferromagnetism for iron above 770° C. and nickel above 340° had been observed. The range of temperatures used, however, was generally small compared with that possible in Curie's experiments of from 25° to 1,370°.

As being most convenient when high accuracy was not aimed at, the Faraday method was adopted. A diagrammatic plan of the specimen magnet part of the apparatus is shown in Fig. 7.

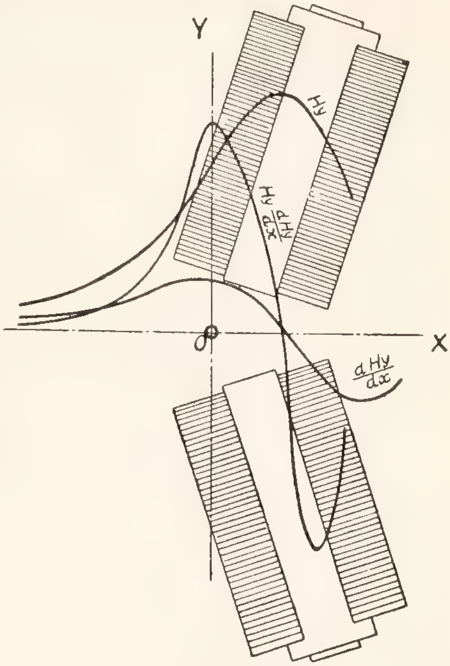


FIG. 7.—Diagram of Curie Arrangement.

For the force along the x axis

$$f = \frac{\kappa}{2}\frac{\partial H_y{}^2}{\partial x}v = m\chi H_y\frac{\partial H_y}{\partial x} \quad . \quad . \quad . \quad . \quad (13)$$

m being the mass of the specimen, and $\chi = \frac{\kappa}{\varrho}$ the mass susceptibility, which, as Curie pointed out, was more fundamental as a characteristic magnetic constant than the volume susceptibility.

The general arrangement of the apparatus is shown in Fig. 8 with the heater removed, the heating oven being represented in Fig. 9.

The substances were placed in a glass, porcelain or platinum vessel, supported on a copper frame, necessarily of rather com-

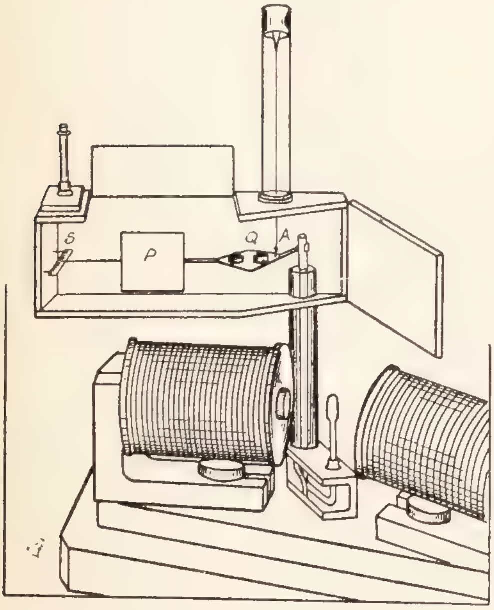


FIG. 8.—Sketch of Curie's Apparatus.

plicated form, connected to one arm of the torsion rod. The suspension (of thin platinum or brass wire) was above OY at a perpendicular distance from OX of about 5½ cm. The plate P acted as a damper, while equilibrium was maintained by moving small weights on the platform Q. As the displacements of the specimen were small (never more than 1·5 mm.) a restoring method was not used, but the displacements themselves were calculated from the movements of the torsion rod pointer over the scale S, readings being taken with a microscope. The distance AS was about 25 cm., and it was possible to take accurate readings corresponding to displacements of the specimen of $\frac{1}{1000}$ mm. The suspensions were calibrated from the times of swing of suspended inertia bars, so that the forces corresponding to any displacement could be calculated. By making use of a distance plate of suitable form pierced with a hole, the specimen holder was always brought into the same position, but the difficulty of ensuring this constituted one of the inherent sources of inaccuracy of the experiment.

The magnetic field H_y was measured by the Weber ballistic method, curves being plotted for H against the current when increasing and decreasing. The direct measurement of $\frac{\partial H_y}{\partial x}$ by moving the coil along OX would have involved measuring a small change in a large quantity; instead the coil with its plane along OY was moved along OY, giving $\frac{\partial H_x}{\partial y}$, which is equal to $\frac{\partial H_y}{\partial x}$ since

$$\frac{\partial H_y}{\partial x} = -\frac{\partial}{\partial x} \cdot \frac{\partial \Omega}{\partial y} = -\frac{\partial}{\partial y} \cdot \frac{\partial \Omega}{\partial x} = \frac{\partial H_x}{\partial y} \quad . \quad . \quad (14)$$

Curves were then drawn for $\frac{\partial H_y}{\partial x}$ and $H_y \frac{\partial H_y}{\partial x}$ (see Fig. 7) and the specimen was arranged at the region where $H_y \frac{\partial H_y}{\partial x}$ was a maximum, so that small errors in the adjustment of its position were of less account. It should be noted, however, that it was difficult to be certain exactly as to the corresponding points for H and $\frac{\partial H}{\partial x}$ owing to the finite dimensions of the search coils.

The heating oven consisted of a porcelain tube *p* (Fig. 9) round which was wound a double filament of platinum wire. A larger porcelain tube P surrounded this, the interspace being filled with kaolin or calcined magnesia. Outside this was a water-jacket screen. The thermocouple was calibrated from the melting-points of salts and metals. The temperature could be kept constant to a tenth of a degree, but the temperature of the specimen (owing to inequalities of temperature over the oven) was not known accurately—at the higher temperatures only within 10° or 20°.

Considering the various uncertainties, Curie estimated that the susceptibility determinations were in general correct to 1 or 2 per cent. Water was used as a standard to check the working of the apparatus, its susceptibility being taken as $\chi = -\cdot 79 \times 10^{-6}$ (this is now known to be too high; the present accepted value being $-\cdot 72 \times 10^{-6}$). Corrections were made throughout for the magnetism of the air, these being calculated from direct determinations on oxygen. Small amounts of impurity in the materials would only affect the results appreciably if they were ferromagnetic; and Curie points out that small traces of iron could be detected by the hysteresis effect to which they gave rise.

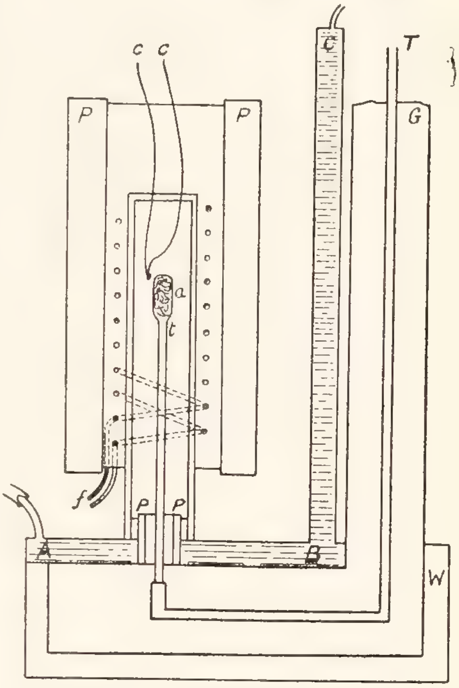


FIG. 9.—The Heating Oven.

P, *p*, porcelain tubes; *f*, heating filament; *a*, containing vessel; *t*, porcelain rod; T, metallic frame connected to torsion arm; *c*, thermocouple; A, B, C, water-jacket; W, G, casing of wood and glass.

Curie's main results are summarized in Table II. A number of special points will be considered.

Diamagnetics.—Water was investigated by placing it in a tube about 1 cm. in diameter; after measuring the force, the water was allowed to evaporate slowly; a blank experiment was then performed; it was then possible to deduce the susceptibility of pure water, the effect of dissolved impurities being eliminated. The mean result of $-\cdot 79 \times 10^{-6}$ was estimated as correct to 3 per cent., and all other values were referred to this. (In the light of later work all Curie's values should therefore be multiplied by $\frac{\cdot72}{\cdot79} = \cdot91$.)

For almost all the diamagnetics investigated there was practically no change in mass susceptibility with temperature. KNO_3 and yellow phosphorus showed no change in passing through their melting-points (310° and 44° respectively). The susceptibilities of different allotropic forms of sulphur were the same, but that of red phosphorus was lower than that of yellow.

Bismuth showed peculiar characteristic properties, the susceptibility diminishing linearly with the temperature up to the melting-point (273°) according to the formula

$$10^6\chi_t = 10^6\chi_{20}\,[1 - \alpha(t - 20)] \quad . \quad . \quad . \quad (15)$$

where $10^6\chi_{20} = 1{\cdot}35$, $\alpha = \cdot00115$

At the melting-point the susceptibility value diminished abruptly from $\cdot957 \times 10^{-6}$ for the solid to a value $\frac{1}{25}$ as great for the liquid.

Paramagnetics.—Oxygen was investigated over a range from 20° to 450°. A small bulb was filled with the gas at some 18 atmospheres pressure and the force measured; the point of the bulb was opened and a second experiment was performed with the gas at atmospheric pressure.

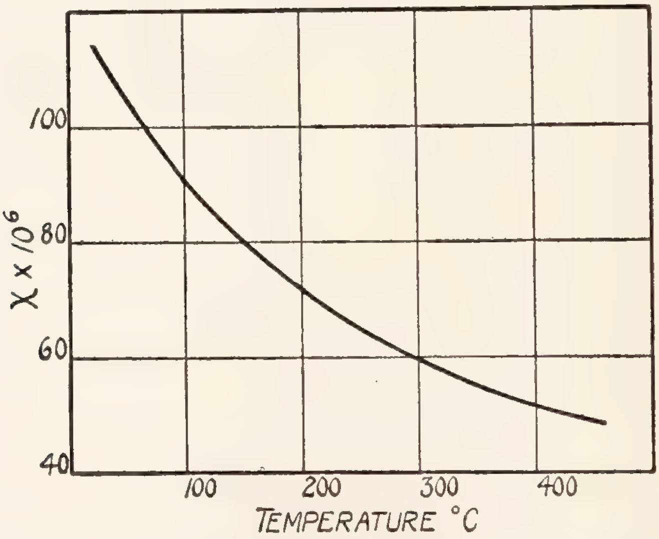


FIG. 10.—Specific Susceptibility of Oxygen.

The results are shown in Fig. 10 and it was found that they could be represented by

$$10^6\chi_T = \frac{33{,}700}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

where T is the absolute temperature. (From this result it may easily be calculated that, neglecting the small magnetic effect of the nitrogen, for air $10^6\chi = \frac{7{,}470}{T}$ and $10^6\kappa = \frac{2{,}640}{T^2}$; the value for air was also found directly with satisfactory agreement.)

The discovery of this variation inversely as the absolute temperature led Curie to re-examine Wiedemann and Plessner's results; and he found that the law $\chi_T = \frac{A}{T}$ was in good agreement with the observations for paramagnetic solutions—of $FeCl_2$, $FeCl_3$, $NiSO_4$, $Co(NO_3)_2$, etc.—and in approximate agreement with those on the solid salts.

Curie himself investigated $Fe_2(SO_4)_3$ solution from 12° to 108°, which gave $10^6\chi_T = \frac{24{,}200}{T}$ and palladium from 20° to 1,370° $\left(\text{approximately } 10^6\chi_T = \frac{1{,}520}{T}\right)$.

Ferromagnetics.—It is impossible to enter in detail into Curie's researches on ferromagnetics. A considerable amount of work had previously been done, particularly by Hopkinson, at temperatures below the critical values; of this a full account is given in Ewing's book. Curie, however, extended the observations above the critical temperatures. The general nature of his results are well indicated by the curves.

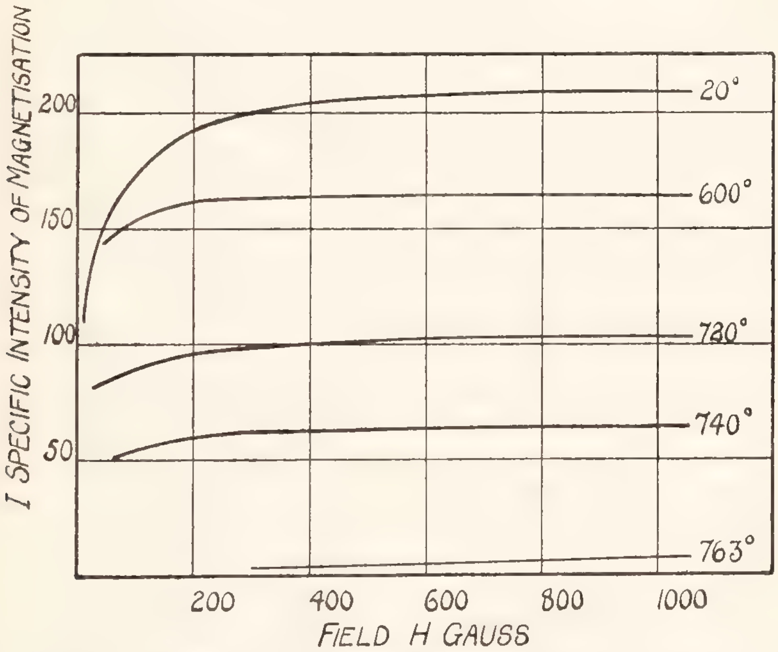


FIG. 11.—Specific Intensity of Magnetization of Soft Iron below 770° C.

Fig. 11 gives the specific intensity of magnetization acquired (the specific intensity being the volume intensity divided by the density, for iron 7·8) at different temperatures by soft iron. The form of the curves gradually changes. From 756–1,375 it is simply a straight line through the origin. The iron has changed from a ferro- to a para-magnetic state. The results are exhibited in a different form in Fig. 12, from which it appears that the transition is not abrupt.

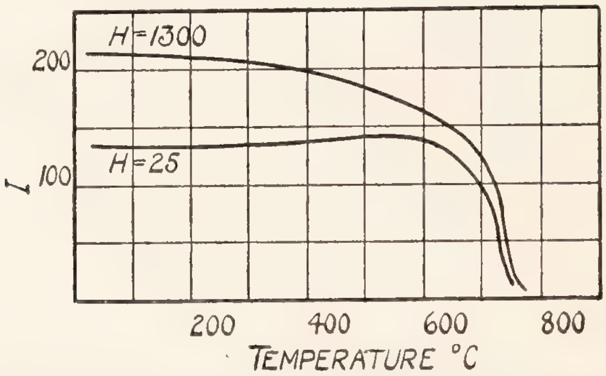


FIG. 12.—Variation of Intensity of Magnetization of Soft Iron with Temperature.

Fig. 13 shows the susceptibility at high temperatures; when the transition range is passed this is independent of the field. The curve was obtained with a field of 1,000 gauss, so the ordinates may also be regarded as giving the specific intensity of magnetization for this field on a scale 1,000 times as great as in Fig. 12.

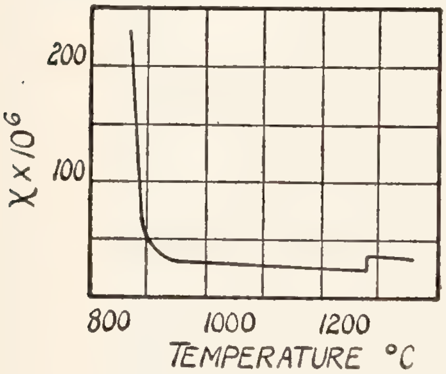


FIG. 13.—Susceptibility of Soft Iron at High Temperatures.

Between 750° and 1,280° there is a decrease in susceptibility with temperature, but at 1,280° there is a sudden increase by about 50 per cent., followed again by gradual decrease.

There is a singularity in the curve also at about 860° which was attributed to the occurrence of allotropic transformation of the iron, which reverted to its normal state again at 1,280°.

The transition for steel and nickel occurred in the regions of 670° and 340°. For magnetite Curie found that the $\frac{1}{T}$ law was approximately followed between 850° and 1,360°.

Conclusions.—The main conclusions to be drawn from Curie's work may now be summarized. For diamagnetics the susceptibility is independent of the field, and generally of the temperature.

Paramagnetic susceptibility is independent of the field and varies, as a first approximation, inversely as the absolute temperature. This generalization

$$\chi = \frac{C}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (17)$$

is known as Curie's law.

Ferromagnetics pass into paramagnetics at higher temperatures.

Substance.	Temperature.	$-10^6\chi$
Bi Solid	20	1·23
Solid	273	·87
Bi Liquid	273–405	·035
P (Yellow) Solid	19–44	·84
P (Yellow) Liquid	44–71	
P (red)	20–275	·66
Water*	15–189	·72
NaCl	16–455	·53
KCl	18–465	·50
K_2SO_4	17–460	·39
KNO_3 Solid	18–310	·30
KNO_3 Liquid	310–420	
SiO_2	18–430	·40
S	15–225	·46
Se	20–200	·29
	240–415	·28
Te	20–305	·28
Br	20	·37
I	18–164	·35

1. *Diamagnetics*

Substance.	Temp.	$10^6\chi$.
Oxygen	20	105
	452	42·5
Air	20	24·4
Pd	20	4·8
	1,370	·79

2. *Paramagnetics*

Field. H gauss.	Temp.	$10^6\chi$.
25	20	4,950,000
1,300	20	151,000
25–1,300	1,000	25·2

3. *Iron*

TABLE II.—MASS SUSCEPTIBILITIES (CURIE).

* Curie's results are all primarily relative to water, for which he obtained $10^6\chi = -\cdot 79$. In the text, values given are taken directly from Curie's paper, but in the above table his results have been recalculated on the basis of the value now accepted for water of $10^6\chi = -\cdot 72$.

Dia- and para-magnetism must thus be fundamentally distinct in origin ; while ferromagnetism is probably to be regarded as a special manifestation of paramagnetism. These experimental conclusions, together with the quantitative results and generalizations as to the effect of temperature, give a basic set of facts which theories of magnetism must attempt to explain.

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CHAPTER IV

THE INTERPRETATION OF MAGNETISM AS AN ATOMIC PHENOMENON

1. Ewing's Theory of Ferromagnetism

As a result of his work on the equivalence of magnetic shells and current circuits, Ampère was led to the suggestion that molecules might behave as magnets owing to a continuous circulation of electric currents in them. Weber (1854) elaborated the idea of molecular circuits and showed that the induction of currents in them by an applied magnetic field would, in accordance with Lenz's law, give rise to an opposing field, this giving a general explanation of diamagnetism. In para- or ferromagnetics, on the other hand, the molecules were supposed to be permanent magnets; ordinarily their axes were distributed at random; and under the influence of an applied field they tended to orientate in the field direction. The molecular-current hypothesis was then, and for long afterwards, highly speculative; but the essential conception, that molecules or atoms could behave as small permanent magnets, is readily interpreted in the light of the modern electron theory, and the results to which it led, particularly in the hands of Ewing, are of permanent value.

In its application to ferromagnetism the molecular magnet hypothesis has to explain the general phenomena of hysteresis, and the earlier attempts were very inadequate. The mere fact that saturation is not attained in weak fields indicates that the molecules must be subject to constraining directive forces. Weber assumed that the magnet axes were distributed at random, and that each molecule was subject to a directive force K, which tended to restore it to its original position. As H increases, I increasing to a maximum value I_0, this leads to the result that I/H is constant until H = K (when $I = \frac{2}{3}I_0$) and subsequently increases more slowly—which is but the roughest approximation to the experimental results, and gives no explanation of hysteresis. Maxwell assumed that the magnets returned to their original position unless the deflection had exceeded a certain value, when a "permanent set" was acquired. Some of the phenomena of hysteresis and residual magnetism were in this way covered, but the postulates were arbitrary. Wiedemann's suggestion of frictional constraints led to difficulties in connection with the finite susceptibility in small fields.

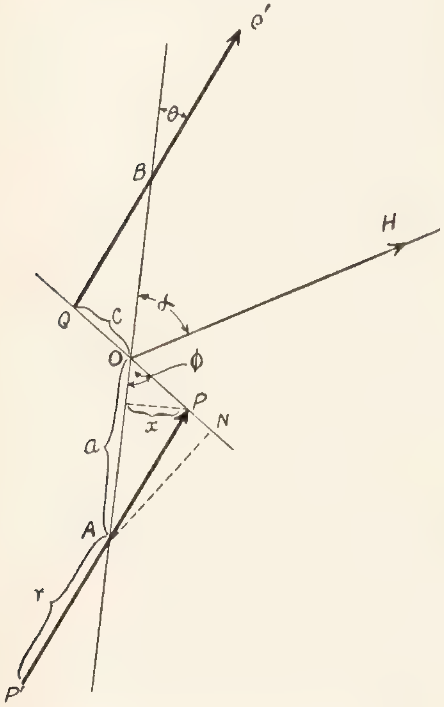

Fig. 14.—Molecular Magnet Pair Group.

The essential feature of Ewing's theory (1890) is that the constraints enter in a natural manner as arising from the forces which the molecules exert on each other in consequence of the fact that they are magnets. The general nature of the results may be readily seen by considering the simplest possible case of a group of two magnets. In the absence of a field they will set themselves along the line of centres AB. Let $2r$ be the length of the magnets, $2a$ the distance between the centres. Under the influence of a small field, equilibrium will be attained when

$$2\mathrm{H}mr\sin(\alpha-\theta)=\frac{m^2\mathrm{AN}}{\mathrm{PQ}^2} \quad . \quad . \quad . \quad . \quad (1)$$

The equilibrium is at first stable, and becomes neutral when

$$\frac{d}{d\theta}\left\{\mathrm{H}\sin(\alpha-\theta)\right\}=\frac{d}{d\theta}\left\{\frac{m}{2r}\cdot\frac{\mathrm{AN}}{\mathrm{PQ}^2}\right\} \quad . \quad . \quad . \quad . \quad (2)$$

When H is increased beyond the limit determined by this equation, the magnets suddenly swing round to a new position of equilibrium, with their axes nearly parallel to the field. The effect on a structure composed of a large number of such pairs, with their lines of centres directed at random, can be readily imagined. On increasing the field from zero there will be at first quasi-elastic deflection, corresponding to the initial part of a magnetization curve; the groups will then successively break up, with rapid resultant increase in magnetic intensity;

and finally there will be a gradual increase as saturation is approached, under the influence of stronger fields. On reducing the field, the magnets will not necessarily retrace the same paths; and when the field becomes zero, although they will resume positions with axes along the lines of centres, those with an original resultant moment opposed to the field will now point in the opposite direction, so that there will be residual magnetism. An explanation can in this way be obtained of the general form of magnetization curves and hysteresis loops. The behaviour of groups of magnets may also be examined experimentally, as has been done by Ewing, giving curves very similar to those obtained for ferromagnetics.

A consideration of a grouping of magnetic molecules in isolated pairs brings out clearly the relevant determinative factors in the processes assumed to occur; but so simple a model would hardly be expected to give a complete representation of the phenomena. In particular, the possible increase in intensity after the groups are broken up until saturation occurs seems too small, while the amount of residual magnetism indicated is much less than that frequently observed. It seems necessary to suppose that the molecules can take up more than one equilibrium position; there must be more than one "line of centres" along which a molecule can set itself. Ewing in fact found that groups of four magnets gave a much closer approximation to the facts; and finally he considered continuous distribution in cubical order. In each group the molecules will normally set themselves along lines of centres, sub-groups being formed with lines of centres (and magnet axes) at right angles to each other. It may be noted that if the groups consist of pairs, or possess purely linear symmetry, each group would normally possess its saturation intensity of magnetization; whereas a group with cubical-order distribution of centres could be unmagnetized. The point is of interest if the groups are regarded as building up constituent crystals of the ferromagnetic material.

On the molecular magnet theory, retentivity depends on the symmetry of the molecular groupings; while coercivity depends on the strength of the molecular ties. There will thus not necessarily be any general relation between them, as is in fact observed. The theoretical retentivity for the simple groupings considered may be easily calculated. An ordinary piece of ferromagnetic material may be supposed to consist of a large number of groups, with lines of centres distributed at random. After a field is applied to produce saturation and then gradually reduced to zero, the molecular magnets in each group will be left directed along the line of centres making the smallest angle with the field, and in a sense giving a resultant moment in the field direction. Each group will retain its saturation intensity, the directions of the group moments, however, making various angles with the field; these directions will be distributed at random within a cone whose semi-angle α is determined by the symmetry characteristic of the groups. For groups consisting of pairs of magnets, or with effective lines of centres all parallel, $\alpha = 90°$; while for groups with equally effective lines of centres at right angles, $\alpha = 45°$, since, if θ had been greater than 45° originally, when the field was applied the magnets would have swung round to a more favourable line of centres, making an angle of less than 45° with the field. The residual intensity I_r compared with the saturation intensity I_0 may then easily be calculated for the linear and cubical case. It may be assumed for simplicity that unit volume contains n similar groups of maximum moment μ; then the contribution of one group to I_r is given by $\mu \cos \theta$; while the number of groups with axes within a solid angle $d\omega$ is proportional to $d\omega$.

$$\frac{I_r}{I_0} = \frac{\int_0^\alpha k\mu \cos \theta d\omega}{\int_0^\alpha k\mu d\omega} \text{ where } \int_0^\alpha k d\omega = n \text{ and } d\omega = 2\pi \sin \theta d\theta$$

$$= \frac{\int_0^\alpha \cos \theta \sin \theta d\theta}{\int_0^\alpha \sin \theta d\theta} = \frac{\sin^2 \alpha}{2(1 - \cos \alpha)}$$

$$\frac{I_r}{I_0} = \tfrac{1}{2}(1 + \cos \alpha) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Thus for linear grouping, in which in each group there is only one direction, but opposite senses of "natural" magnetization,

$$\frac{I_r}{I_0} = \cdot 5(1 + \cos 90°) = \cdot 5$$

while for cubical distribution of lines of centres in each group

$$\frac{I_r}{I_0} = \cdot 5(1 + \cos 45°) = \cdot 8536$$

(Ewing obtains ·89, since he virtually assumes one of the planes of centres in each group to lie in the field direction).

These figures may be compared with the values for I_r of about 930 and 420 for a soft-iron wire before and after stretching, another specimen giving 1,120 and 950; the saturation intensity for iron being about 1,700. Although the above treatment can be refined in the light of more recent work, particularly on ferromagnetic crystals, the attack on the problem seems to be on the right lines; and there is obviously room for much further experimental investigation on residual magnetism.

The molecular magnet theory has also been applied by Ewing with considerable success to explain qualitatively many of the complicated phenomena presented by ferromagnetics under the influence of temperature changes, strains and mechanical disturbances. In its original form, however, it is open to several serious objections, one of which will become clear in discussing Weiss's work on intrinsic molecular fields. The objections have been recognized by Ewing himself, and recently he has proposed a modified model of ferromagnetic induction. From the experimental magnetization curves, it is clear that barely 1 per cent. of the whole magnetization of saturation may be acquired during the quasi-elastic stage, so that the second stage of the process, corresponding to the sudden turning of the molecular magnets, must set in, for the most favourably situated groups, when the deflections are small, and also for quite small values of the applied field. Referring to Fig. 14, and equations (1) and (2), it is clear that the pairs to become unstable first will be those for which $(a - \theta) = 90°$ in the limiting position. For these the state of instability is reached when

$$\frac{d}{d\theta}\frac{\mathrm{AN}}{\mathrm{PQ}^2} = 0 \text{ or } \frac{d}{dx}\frac{x}{\mathrm{OP}^3} = 0 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

which, since $\mathrm{OP}^2 = x^2 + (a - r)^2$, gives

$$\tan\phi = \frac{1}{\sqrt{2}}(\phi = 35°\ 16') \text{ or } r\sin\theta = \frac{a - r}{\sqrt{2}} \quad . \quad (4.1)$$

The range of stability is thus small if the "clearance" between the magnets $(2a - 2r)$ is small.

The corresponding value of H is given by

$$\mathrm{H} = \frac{m}{12\sqrt{3}(a - r)^2 \sin a} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and so may be very large for $(a - r)$ small.

If the magnets are supposed to be very close to account for the narrow range of stability, the mutual forces would be some thousand times greater than those which experiment indicates.

A model is required which gives a narrow range of stable deflection with much weaker control. These particular difficulties in the way of the older model are in addition to those which arise if attempts are made to interpret the magnets in terms of the electronic structure of atoms, as the fields arising from orbital electrons at distances of the order of those between atomic centres are much too small to provide adequate control.

The essential feature of Ewing's new model is that the controls are supposed to be provided not primarily by the neighbouring magnetic molecules or atoms, but by other parts of the same molecule (or atom). The "pivoted magnet" is taken to correspond to a disposition of electronic orbits close to the nucleus with a resultant moment; this inner magnetic part of the atom sets itself in a direction controlled by the symmetry of the outer electron orbits. The atom may be represented roughly (as in Fig. 15) by a system of fixed magnets, A–D, having no external resultant moment, with an inner "pivoted magnet" O.

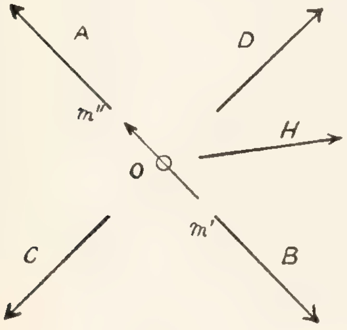

FIG. 15.

The clearance may be very small, giving a narrow range of stable deflection; while the control, depending on the difference of pole strength $m' - m''$, may at the same time be weak. The difference between the effective pole strengths m' and m'' may quite possibly be influenced—much as in the older model—by neighbouring atoms. The model thus explains the possibility of limited ranges of stable deflection without postulating very strong controls; and at the same time seems capable of giving some idea of the reason for the marked influence of impurities and modifications of crystal structure on the character of the magnetization curves. Although the model is crude it is surprisingly suggestive, and it will be referred to later; it may here be mentioned that it seems possible to bring it into close relation with Bohr's picture of the atomic structure of the paramagnetic elements; and also it seems to suggest a way of escape from some of the difficulties connected with orientation—for the idea that magnetic atoms, in solids, can rotate as a whole under the influence of applied fields, seems, at least, highly improbable.

2. Dia- and Para-magnetism. Langevin's Theory

The foundations of the modern electronic theory of magnetism were laid by Langevin in 1905. Curie's work ten years before had provided extensive experimental data, and led to a number of general conclusions. The electron had been discovered, and its nature investigated. The electron theory of matter, developed with great power by Lorentz, was now on a secure experimental basis. Some specific attempts had been made towards an electronic theory of magnetism, but they had not proved very successful. Langevin, however, showed that it was possible to give a precise significance to the old ideas of Ampère and Weber in terms of the electron hypothesis, and to find for dia- and para-magnetism the completely distinct interpretations which they demanded.

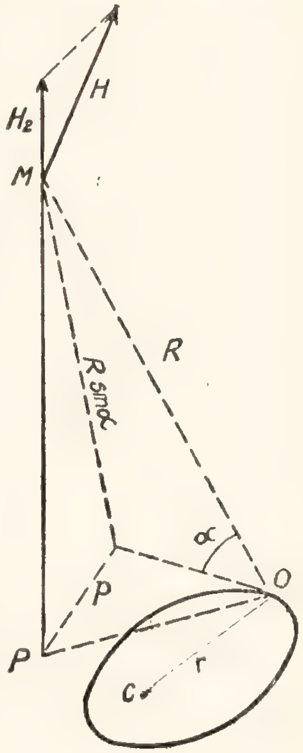

FIG. 16.

The electrons in each molecule are assumed to be moving in closed orbits, producing at a distance magnetic effects similar to those arising from a current circuit. It has already been shown generally (cf. II, 59) that an electron moving in an orbit of area S in a periodic time τ produces at a distance the same mean magnetic field as a magnet of moment μ such that

$$\mu = \frac{eS}{c\tau}.$$

This will now be proved for a special case in a direct and simple manner. Consider the field produced at M (see Fig. 16) by an electron moving in an orbit under the influence of central forces from C. The field H_z will depend purely on the projected orbit on a plane perpendicular to MP, any velocity perpendicular to this plane giving rise only to components perpendicular to H_z.

Let v (direction OQ) be the velocity of the electron at O. Then H (at right angles to the plane OQM) is given by

$$H = \frac{ev \sin \alpha}{cR^2}$$

$$\frac{H_z}{H} = \frac{p}{R \sin \alpha}$$

$$H_z = \frac{epv}{cR^3}$$

Let A be the areal velocity of the electron referred to P. Then

$$H_z = \frac{2eA}{cR^3}$$

If R is large compared with r, S the projected area of the orbit, and τ the time of revolution, the mean value of H_z is thus given by

$$H_z = \frac{2eS}{c\tau R^3}$$

so that the mean field is equivalent to that produced by a magnet of moment μ where

$$\mu = \frac{eS}{c\tau} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

A projected orbit has here been considered, and a particular component of the field; but the argument may easily be extended; the general result, as before, being that the effective magnetic moment, both in magnitude and direction, is given by

$$\boldsymbol{\mu} = \frac{eS}{c\tau}\mathbf{n}_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6.1)$$

The variable part of the field is, of course, neglected simply because mean effects are being considered. This, however, implies that radiational effects are neglected, which gives the procedure deeper justification (experimentally), for radiation, involving loss of energy, is incompatible with the existence of stable orbits.

In a molecule or atom the moments corresponding to each orbital electron will add their effects and there may or may not be a resultant magnetic moment according to the symmetry of the structure. In any case, the creation of an external field will modify the orbital motion in a sense to produce a diamagnetic effect; but if the molecule has a resultant moment there is a possibility of orientation occurring, producing a paramagnetic effect, which, in general, will mask completely the initial diamagnetism.

Diamagnetism.—When an external field is applied it may be assumed to acquire its final value in a time which is long compared with the periodic time of an electron in its orbit. The variation of magnetic flux through the orbit will produce an electric force round it in accordance with the fundamental electromagnetic generalizations (II, 38–41) and the electron will be accelerated or retarded.

Consider an electron moving round an orbit s, of area S; let r be the radius measured from the centre of force, and v the resolved velocity at right angles to r, so that rv is constant, while r and v may be variable; and as element of area take $dS = \frac{1}{2}rds'$; suppose for simplicity that the field H is applied perpendicularly to the orbit. The result generally will apply to the projected orbit perpendicular to the field. Then, using (6) and (II, 40)

$$\frac{d\mu}{dt} = \frac{d}{dt}\frac{evr}{2c} = \frac{Ee^2r}{2mc}$$

Now

$$\int E ds' = \int -\frac{1}{c}\frac{dH}{dt}dS = -\frac{1}{2c}\int r\frac{dH}{dt}ds'$$

$$d\mu = -\frac{e^2r^2}{4mc^2}dH$$

$$\Delta\mu = -\frac{e^2r^2}{4mc^2}H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7$$

r^2 in this expression is a mean value for the orbit. Since μ may be written $\mu = \frac{e\omega r^2}{2c}$, the change in the moment may be considered as brought about by an increase o in the angular velocity given by

$$o = -\frac{eH}{2mc} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

This result (8) has been derived here for a special case by a method which makes no claim to rigour; but it can be shown to hold quite generally. Let T be the kinetic, U the potential energy of a charge in an atom, and let L = T − U. Then, in the absence of external fields, the general equation of motion is

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{x}} - \frac{\partial L}{\partial x} = 0.$$

When an external field is applied

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{x}} - \frac{\partial L}{\partial x} = e\left(\mathbf{E} + \frac{\mathbf{v} \times \mathbf{H}}{c}\right)_x$$

and this may be shown to reduce to

$$\frac{d}{dt}\frac{\partial L'}{\partial \dot{x}} - \frac{\partial L'}{\partial x} = 0$$

if L′(= T′ − U′) is measured with reference to co-ordinates rotating about H with an angular velocity

$$\mathbf{o} = -\frac{e}{2mc}\mathbf{H} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8.1)$$

In the new co-ordinate system everything then proceeds (as far as the particular charge is concerned) exactly as before, so that the effect of the external field is simply to give the charge an additional angular velocity about the centre of force round which it moves, and in the direction of the magnetic field. It will be noticed that the "Larmor precession" velocity, o, is the same for all charges for which e/m is the same; and it must not therefore be supposed that an atom as a whole precesses with this angular velocity; all the electrons will precess in a similar manner; but the positive nucleus, with a much smaller e/m, will precess (about the common centre of the whole atomic system) much more slowly, and of course in the opposite direction. The Larmor precession is of great importance in the treatment of the Zeeman effect, this and diamagnetism being different aspects of the same phenomenon.

(7) gives the moment acquired by each electron in the atom as a result of the application of the field; and the atomic diamagnetic susceptibility is obtained by summation of the expression for over all the N electrons in the atom, giving

$$\chi_{At} = -\frac{e^2}{4mc^2}\sum_{N}\overline{r^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (9)$$

where $\overline{r^2}$ is the projected value perpendicular to H. The smallness of the diamagnetic susceptibility at once follows from the smallness of r; it will be seen subsequently that estimates of atomic magnitudes on the basis of (9) agree in order of magnitude with those deduced by other methods.

Considering an element of volume, or a single molecule, its diamagnetic state depends at each instant solely on its position relative to the field; collisions between molecules will have no effect on the susceptibility. Moreover, as the diamagnetic effect depends primarily on the structure of the atoms themselves, which will be practically unaffected by temperature changes, the diamagnetic susceptibility should vary very little with the temperature, as was found by Curie; it should also vary little with the physical state of the substance, again in agreement with Curie's results. The theoretical interpretation thus gives significance to Curie's generalizations, and at the same time enhances the interest of the exceptions.

In investigating the change in the magnetic moment of an orbit induced by the field, it was unnecessary to consider separately whether the orbit was deformed, that is whether there was any change in r.

Suppose the electron is moving under the influence of a central force so that

$$m\omega^2 r = f(r) \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

It has already been shown that when an external field H is established

$$\Delta\mu = -\frac{e^2 r^2}{4mc^2}\mathrm{H}$$

and since

$$\Delta\mu = \frac{e}{2c}\Delta(\omega r^2)$$

$$r^2\Delta\omega + 2\omega r\Delta r = -\frac{er^2}{2mc}\mathrm{H} \quad . \quad . \quad . \quad . \quad (11)$$

When a field is applied there will be a magnetic force $\frac{1}{c}\mathrm{H}e\omega r$, and the equilibrium equation (10) becomes

$$\frac{1}{c}\mathrm{H}e\omega r + m(\omega + \Delta\omega)^2(r + \Delta r) = f(r + \Delta r) \doteqdot f(r) + f'(r)\Delta r$$

Retaining only first-order terms, and substituting from (10) and (11)

$$\{f'(r) + 3m\omega^2\}\,\Delta r = 0 \quad . \quad . \quad . \quad . \quad . \quad (12)$$

This gives $\Delta r = 0$, and (from 11) $\Delta\omega = -\dfrac{e\mathrm{H}}{2mc}$ (as in 8)

except when $\quad f'(r) = -3m\omega^2 = -3\dfrac{f(r)}{r}$

that is when $f(r) = \dfrac{c}{r^3}$.

When the attractive force varies inversely as the cube of the distance Δr is indeterminate from the above equations; but it seems legitimate to suppose that in this very special case also $\Delta r = 0$, so that quite generally, in accordance with (8·1), the effect of the establishment of a magnetic field is to produce simply a precessional motion without any change in the form of the orbit.

Paramagnetism.—The diamagnetic effect will occur whether the molecules or atoms have a resultant moment or not; if they have a resultant moment μ there is a possibility of a second effect, due to the tendency of the molecular magnets to turn in such a direction that their potential energy in the field is a minimum. This orientation, however, cannot be produced *directly* by the field, as the torque exerted by it only gives rise to the precessional motion. The potential energy of a magnet relative to the field is $-\mu H \cos\theta$ (II, 18). When a field is applied the molecules will acquire different energies according to the direction of their axes, and a uniform distribution will no longer be compatible with temperature equilibrium. There will be a tendency for a change to take place in the relative numbers of molecules with axes pointing in different directions, so that there will be a greater number in positions of lower potential energy—that is, with their axes pointing in the field direction. The changes in orientation involved can only be brought about by those processes by which temperature equilibrium is maintained, that is primarily by mutual collisions.

The question may be attacked thermodynamically, considering the case of a gas. If the gas acquires a moment dM the quantity dQ of heat which must be removed from it to maintain the temperature constant is given by

$$dQ = H\,dM$$

$$T\,d\phi = H\left(\frac{\partial M}{\partial H}dH + \frac{\partial M}{\partial T}dT\right)$$

Now
$$\frac{\partial}{\partial T}\frac{\partial \phi}{\partial H} = \frac{\partial}{\partial H}\frac{\partial \phi}{\partial T}$$

$$\therefore \frac{\partial M}{\partial T} = -\frac{H}{T}\frac{\partial M}{\partial H}$$

$$M = f\left(\frac{H}{T}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

The form of f cannot be determined; but if the moment acquired is proportional to the field—that is, if the susceptibility is constant at a given temperature,

$$M = k\frac{H}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13.1)$$

and, in accordance with Curie's law, the susceptibility varies inversely as the absolute temperature.

A paramagnetic gas may be treated on the basis of statistical kinetic theory. It will be assumed that each molecule has a moment μ. Assuming equipartition of energy, the number of molecules with axes pointing in a direction θ to the field, per unit solid angle, when equilibrium is attained will be proportional to $e^{-\frac{E}{kT}}$ where k is the Boltzmann constant (per molecule), so that $kT = \frac{2}{3}(\frac{1}{2}mv^2)$, v^2 being the mean square velocity of thermal agitation, and $E = -\mu H \cos\theta$. The results obtained would only be expected to be correct in so far as there is equipartition of energy between the degrees of freedom, the molecule in particular being supposed to possess mean rotational energies about axes perpendicular to μ, equal to $\frac{1}{2}kT$. It is the rotations about these axes which check the tendency to alignment in the field direction. For oxygen, at ordinary temperatures, the specific heat indicates that there are two degrees of rotational freedom, to each of which may be attributed an energy $\frac{1}{2}kT$, in accordance with the requirements; but, as will be seen subsequently, the treatment adopted would not be expected to be generally applicable. It should also be noted that the rotation of the electron about the magnetic axis which gives rise to the magnetic moment is supposed not to be subject to thermal variation.

The paramagnetic susceptibility of a gas in which the necessary conditions are fulfilled may now be calculated. Consider a volume containing n molecules. For the number with axes within a solid angle $d\omega$

$$dn = Ce^{\frac{\mu H \cos\theta}{kT}} d\omega$$

$$= Ce^{a\cos\theta} d\omega \text{ where } a = \frac{\mu H}{kT}$$

The distribution of axes will be symmetrical about the field direction, and for $d\omega$ may be taken $2\pi \sin\theta d\theta$ (this being the solid angle between two cones with semi-vertical angles differing by $d\theta$) where θ may vary from 0 to π. Then, for the resultant magnetic moment M in the field direction, writing $\bar{\mu}$ for the mean effective molecular magnetic moment,

$$M = n\bar{\mu} = \int_0^\pi Ce^{a\cos\theta}.2\pi \sin\theta d\theta.\mu\cos\theta \quad . \quad . \quad (14)$$

while

$$n = \int_0^\pi Ce^{a\cos\theta}.2\pi \sin\theta d\theta$$

$$= 2\pi C \int_{-1}^{+1} e^{ax} dx$$

$$n = \frac{2\pi C}{a}(e^a - e^{-a}) = \frac{4\pi C}{a} \sinh a \quad . \quad . \quad (14.1)$$

$$M = 2\pi\mu C \int_0^\pi e^{a\cos\theta} \sin\theta \cos\theta \, d\theta$$

$$= 2\pi\mu C \int_{-1}^{+1} xe^{ax} dx$$

Now
$$\int_{-1}^{+1} x e^{ax} dx = \left[\frac{x e^{ax}}{a}\right]_{-1}^{+1} - \left[\frac{e^{ax}}{a^2}\right]_{-1}^{+1}$$
$$= \frac{1}{a}(e^{a} + e^{-a}) - \frac{1}{a^2}(e^{a} - e^{-a})$$
$$= \frac{2}{a}\cosh a - \frac{2}{a^2}\sinh a.$$

Substituting from (14) for C

$$\frac{\mathrm{M}}{\mu n} = \frac{\bar{\mu}}{\mu} = \coth a - \frac{1}{a} \quad . \quad . \quad . \quad . \quad . \qquad (15)$$

This result is in accordance with (13).

Writing coth a in exponential form, and expanding, when a is small (that is H/T is small) (15) becomes

$$\frac{\mathrm{M}}{\mu n} = \frac{\bar{\mu}}{\mu} = \frac{a}{3} - \frac{a^2}{45} + . \; . \; . \quad . \quad . \quad . \quad . \qquad (15.1)$$

while if a is large

$$\frac{\mathrm{M}}{\mu n} = \frac{\bar{\mu}}{\mu} = 1 - \frac{1}{a} + 2e^{-2a} + . \; . \; . \quad . \quad . \quad . \qquad (15.2)$$

The function $\mathrm{L}(a) = \left(\coth a - \frac{1}{a}\right)$ is plotted in Fig. 17.

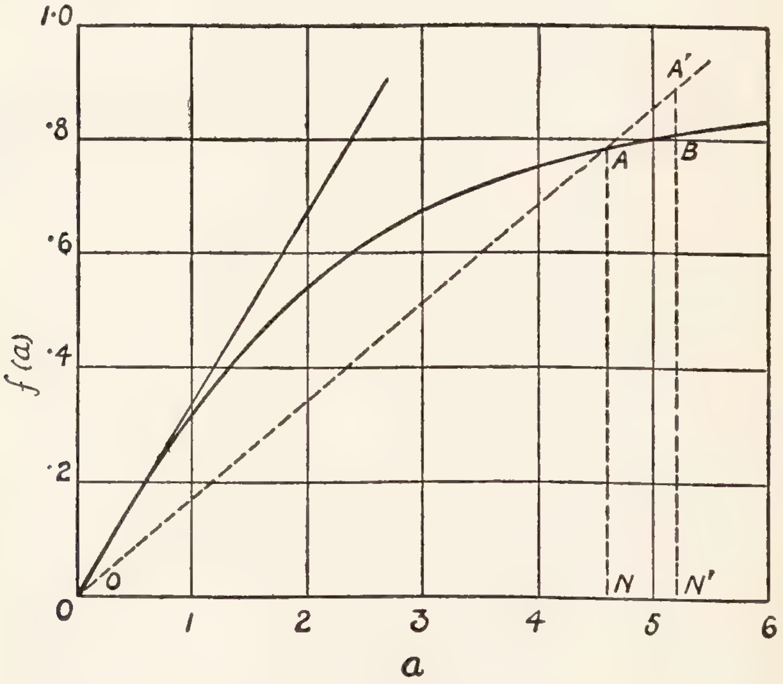

FIG. 17.

For the curve, $f(a) = \coth a - \frac{1}{a}$ For the tangent at O, $f(a) = \frac{a}{3}$

The quantitative deductions as to molecular magnetic moments will be considered in detail later; but it is desirable to have some idea of the order of magnitude of a to see how far the approximation of (15.1) is justifiable. For iron (atomic weight $A = 55{\cdot}8$, density $= 7{\cdot}8$) the saturation intensity (per unit volume) is of the order 1,700. Using N for Avogadro's number, so that $Nk = R = 8{\cdot}3 \times 10^7$ ergs per degree,

$$a = \frac{\mu H}{kT} = \frac{N\mu}{Nk}\left(\frac{H}{T}\right) = \frac{1{,}700 \times 55{\cdot}8}{7{\cdot}8 \times 8{\cdot}3 \times 10^7}\left(\frac{H}{T}\right)$$
$$\doteqdot (1{\cdot}5 \times 10^{-4})\frac{H}{T}.$$

At ordinary temperatures, therefore, even with the highest fields available, a will be so small that it will be sufficient to take only the first term in (15.1)

$$\frac{M}{\mu n} = \frac{\bar{\mu}}{\mu} = \frac{a}{3} \quad M = \frac{n\mu^2 H}{3kT} \quad \bar{\mu} = \frac{\mu^2 H}{3kT} \quad . \quad . \quad (15.3)$$

For ordinary paramagnetics there will be no approach to saturation, the magnetization acquired, corresponding to the initial part of the $\left(\coth a - \frac{1}{a}\right)$ curve, being directly proportional to the field. (In ferromagnetics there are mutual actions between the molecules, and the phenomena become quite different; iron was considered simply as enabling an estimate of the order of magnitude of magnetic moments to be formed.)

From (15.3)

$$\kappa_v = \frac{M_v}{H} = \frac{n_v \mu^2}{3kT} \text{ and } \chi_m = \frac{n_m \mu^2}{3kT} \quad . \quad . \quad . \quad (15.4)$$

n_v and n_m being the number of molecules per unit volume and unit mass respectively. Considering unit volume of a gas, $p = n_v kT$ so that

$$\kappa_v = \frac{(n_v \mu)^2}{3p} = \frac{I_0^2}{3p} \quad . \quad . \quad . \quad . \quad . \quad (15.5)$$

where I_0 is the saturation intensity per unit volume.

The theoretical conclusion, therefore, that the paramagnetic susceptibility should vary inversely as the absolute temperature, is completely in accordance with Curie's generalization. The theory only applies to cases where the mutual magnetic influence of the molecules may be neglected—it is essentially a theory of a paramagnetic gas—but from the fact that the law deduced holds widely, it may be concluded that the mutual magnetic influence of the molecules is frequently negligible. An essentially important result of Langevin's theory is that, as will be seen from any of the equations (15), the saturation intensity, and hence the molecular, or atomic, moment, may be deduced from measurements in small fields; and that if I/I_0 is plotted against a, the resultant curve should be the same for all "normal" paramagnetic substances.

The result for a small, as expressed in (15.3), is of such general application, that it seems desirable to derive it specially, as this can be done very simply, making the assumption that a is small initially.

For a small, $e^{a \cos \theta} = 1 + a \cos \theta$.

$$M = \int_0^\pi C(1 + a \cos \theta) 2\pi \sin \theta d\theta . \mu \cos \theta$$

$$n = \int_0^\pi C(1 + a \cos \theta) 2\pi \sin \theta d\theta \quad . \quad . \quad . \quad . \quad . \quad (16)$$

$$\frac{M}{\mu n} = \frac{\int_0^\pi \sin \theta \cos \theta d\theta + a \int_0^\pi \cos^2 \theta \sin \theta d\theta}{\int_0^\pi \sin \theta d\theta + a \int_0^\pi \sin \theta \cos \theta d\theta} \quad . \quad . \quad . \quad (16.1)$$

$$= a \frac{\int_0^\pi \cos^2 \theta \sin \theta d\theta}{\int_0^\pi \sin \theta d\theta} = \frac{a}{3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16.2)$$

$$\frac{I}{I_0 a} = \overline{\cos^2 \theta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16.3)$$

the bar denoting a spatial mean value. This spatial mean value is $\frac{1}{3}$ if any orientation is possible, as above; but if only certain discrete orientations are possible a different value will be obtained.

The general conclusions from Langevin's work may be briefly summarized. It is possible to form a simple and exact conception of the phenomena of para- and dia-magnetism on the basis of electronic currents in molecules. The establishment of an external field results in a modification of the currents in a sense to produce a diamagnetic effect; if the initial molecular magnetic moment is zero, the substance will be diamagnetic in the ordinary sense; and the susceptibility will be, as a first approximation, independent of temperature and physical state. When the molecules have a moment differing from zero, there will be the initial diamagnetic effect ; but a paramagnetic effect will eventually be produced as a result of a change, brought about by collisions, in the orientation distribution of molecules, the distribution immediately after the field is applied being incompatible with thermal equilibrium. For feebly paramagnetic substances, the susceptibility should vary, in accordance with Curie's law, inversely as the absolute temperature.

3. The Molecular Field Theory of Weiss

In Langevin's theory of paramagnetism, virtually an ideal paramagnetic gas is considered, and it is assumed that the mutual effect of the elementary magnets would be negligible. Weiss extended the treatment so as to include paramagnetics generally, and in particular ferromagnetics, by postulating the existence of a " molecular field " proportional to the intensity of magnetization acquired. The effective field H acting on any molecule can then be regarded as the sum of the external field H_e and the internal field proportional to I so that

$$H = H_e + NI \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

If the field NI is regarded as arising from the magnetic effect of the surrounding molecules (as in Ewing's theory) the order of magnitude of the coefficient N may be easily calculated. Consider a molecule in the interior of a uniformly magnetized medium, and suppose that the matter in a small sphere, with centre at the molecule, is removed ; the magnetic potential Ω and the field H_i at the centre due to the equivalent surface density of magnetization on the sphere may be calculated from Poisson's Theorem (II, 16). For the potential at a small distance x from the centre of the sphere, assuming I is in the x direction, r being the radius of the sphere,

$$\Omega_x = -\iint \frac{I \cos \theta dS}{(\text{[illegible]} - x \cos \theta)} = C - \frac{4}{3}\pi I x$$

so that
$$H_i = -\frac{\partial \Omega}{\partial x} = \frac{4}{3}\pi I \quad . \quad . \quad . \quad . \quad . \quad (17.1)$$

On filling up the sphere, if the molecular magnets are arranged in some regular cubical manner, or if they are distributed completely at random, the resultant additional effect will be zero ; the calculation of the exact effect would involve a knowledge of the distribution of the molecules ; in any case, however, (17.1) may be regarded as giving an approximate value for the molecular *magnetic* field. It will be seen later that the value $\frac{4}{3}\pi$ for N is in many cases thousands of times too small to account for the observed results; the formally simple hypothesis of a molecular field proportional to intensity, however, in conjunction with Langevin's theory, does lead to conclusions in striking accord with experiment, if the proportionality factor is regarded as a constant to be determined.

In this section, therefore, some of the consequences of (17) will be considered, and put in a form convenient for comparison with experiment; but no specific assumption will be made as to the nature of the molecular field.

Weiss assumes that the molecules in a ferromagnetic solid are subject to no other constraints, as regards rotation, than those arising from the molecular field; apart from this, the rotations are as unrestricted as those in a gas. (It may be useful to introduce the term "carriers" for the atoms or molecules or parts of them, which constitute the elementary magnets; Weiss's assumption essentially implies that the carriers are free to rotate.)

Paramagnetic phenomena generally should then be determined by the two equations (15) and (17).

$$H = H_e + NI \quad \ldots\ldots \quad (17)$$

$$\frac{I}{I_0} = \coth a - \frac{1}{a} \quad \ldots\ldots \quad (18)$$

where

$$a = \frac{\mu H}{kT} \quad \ldots\ldots \quad (18.1)$$

Where there is no external field acting, the possibility arises of a ferromagnetic substance being spontaneously magnetized. Let ϱ be the density of the substance, m the molecular weight, σ_m the magnetic moment per gram molecule, and σ_{m_0} the saturation moment.

Then

$$a = \frac{\mu H}{kT} = \frac{\sigma_{m_0} H}{RT}$$

In the absence of an external field (17) becomes

$$H = NI = N\frac{\varrho\sigma_m}{m} \quad \ldots\ldots \quad (19)$$

$$\frac{\sigma_m}{\sigma_{m_0}} = \coth a - \frac{1}{a} \quad \ldots\ldots \quad (20)$$

$$a = \frac{N\varrho\sigma_m\sigma_{m_0}}{mRT} = \frac{N\varrho\sigma_{m_0}{}^2}{mRT}\cdot\frac{\sigma_m}{\sigma_{m_0}} \quad \ldots \quad (20.1)$$

(20.1) may be written

$$\frac{\sigma_m}{\sigma_{m_0}} = \frac{mRT}{N\varrho\sigma_{m_0}{}^2}a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (21)$$

The simultaneous equations (20) and (21) may most easily be solved graphically, as in Fig. 17, (21) being represented by the dotted line whose slope will depend on T. The curves cut at O and A so that, as solutions of (20) and (21), $\sigma_m/\sigma_{m_0} = 0$ or NA. It may easily be seen, however, from a consideration of the curves, that the state of magnetization at A is stable, that at O unstable. If, for example, at A, σ_m/σ_{m_0} is artificially increased to the value N′A′, the increase in a being NN′, the ratio of the new field to that required to maintain equilibrium is as N′B to N′A′; and the state will revert to that represented by A. At O, on the other hand, a small increase in intensity of magnetization will give rise to fields which result in still further increase, until A is reached.

From the Figure it is clear that spontaneous magnetization will only occur if the slope of OA is less than that of the tangent at the origin, that is less than $\frac{1}{3}$.

The condition for spontaneous magnetization then is

$$\frac{\sigma_m}{\sigma_{m_0}} < \frac{1}{3}a$$

or, substituting from (21),

$$T < \frac{\sigma_{m_0}{}^2 N\varrho}{3mR} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (22)$$

This temperature, θ, may be regarded as a transition temperature above which the substance becomes paramagnetic. At θ the thermal motions become sufficiently vigorous to overcome the tendency towards alignment of the carriers; as would be anticipated, θ is greater the greater the moment of the carriers, and the greater the molecular field coefficient.

For ferromagnetics, as for paramagnetics generally, complete saturation, corresponding to perfect alignment of the elementary magnets, would only occur for fields of enormous magnitudes; but below the transition-point, there will be a quasi-saturation at any particular temperature corresponding to the ordinate of the point where the dotted line and the Langevin curve of Fig. 18 cut each other. This quasi-saturation value, attained primarily under the influence of the intrinsic molecular field, will approach more nearly the true saturation value the lower the temperature.

Let $\theta = \frac{\sigma_{m_0}{}^2 N\varrho}{3mR}$, and let σ_m be the quasi-saturation moment per gram molecule at temperature $T < \theta$.

Then from (21)

$$\frac{\sigma_m}{\sigma_{m_0}} = \left(\frac{T}{\theta}\right)\frac{a}{3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (23)$$

and since from (20)

$$\frac{\sigma_m}{\sigma_{m_0}} = \coth a - \frac{1}{a}$$

$$\frac{T}{\theta} = \frac{3}{a}\left(\coth a - \frac{1}{a}\right)$$

Thus (23) may be written

$$\frac{\sigma_m}{\sigma_{m_0}} = f\left(\frac{T}{\theta}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (24)$$

$\frac{\sigma_m}{\sigma_{m_0}}$ for any value $\left(\frac{T}{\theta}\right)$ may be found graphically from the point of intersection of a line OA (Fig. 17) of slope $\frac{1}{3}\left(\frac{T}{\theta}\right)$ with the Langevin curve, and hence $\frac{\sigma_m}{\sigma_{m_0}}$ obtained as a function of $\frac{T}{\theta}$; the explicit expansion of $f\left(\frac{T}{\theta}\right)$ being somewhat untractable. The theoretical curve is shown in Fig. 18, and also observed values, which will be discussed in Chapter VI.

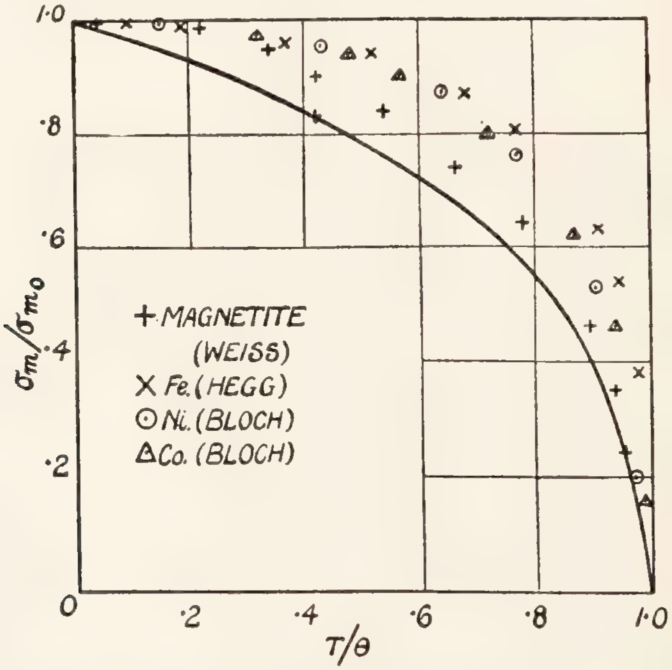

FIG. 18.

$\frac{\sigma_m}{\sigma_{m_0}}$ as a function of $\frac{T}{\theta}$

The essential point to be noticed is that, according to Weiss's theory, the form of the curve, plotted in this way for "corresponding" temperatures, should be the same for all substances; and this, to a first approximation, is strikingly confirmed by experiment, though there are wide divergences from the theoretical curve. It should be noted, however, that the theory assumes σ_{m_0}, and hence the effective molecular moment μ, to be independent of the temperature.

Above the Curie point spontaneous magnetization no longer occurs. The substance becomes paramagnetic and at temperatures not too near the transition temperature μH (where $H = H_e + NI$) is small compared with kT. Under these conditions

$$a = \frac{m_0}{RT}\left(H_e + N\frac{\varrho\sigma_m}{m}\right) \quad . \quad . \quad . \quad . \quad . \quad (25)$$

$$\sigma_m/\sigma_{m_0} = \coth a - \frac{1}{a} \fallingdotseq \frac{a}{3} \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

$$\chi_m = \sigma_m/H = \frac{(\sigma_{m_0}{}^2/3RT)}{1 - N\varrho\sigma_{m_0}{}^2/3mRT} \quad . \quad . \quad (27)$$

$$= \frac{\sigma_{m_0}{}^2}{3R(T - \theta)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27.1)$$

where, as before,

$$\theta = \frac{\sigma_{m_0}{}^2 N\varrho}{3mR} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

Above the Curie point ferromagnetics therefore should follow a modified Curie law—Weiss's law,

$$\chi_m = \frac{C_m}{T - \theta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27.2)$$

where C_m—the Curie constant per gram molecule—as in the expression $\chi_m = C_m/T$ for normal paramagnetics, is given by

$$C_m = \sigma_{m_0}{}^2/3R \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

It may be noted here that many paramagnetics which do not obey Curie's law are found to follow (27.2) very closely; but θ is frequently negative—the transition point is "virtual." As may be readily seen from (28) this corresponds to a negative value of N, or a negative molecular field.

Observations on ferromagnetics above the Curie point enable the constants in (27.2) to be determined, and hence, using (28) and (29), both σ_{m_0} and N may be found.

At temperatures close to θ, (27.2) will no longer be expected to hold, for NI may be relatively large, and a, in consequence, may be too great to justify the approximation of (26). By an appropriate manipulation of the equations it may be shown that, in the immediate neighbourhood of the Curie temperature, σ_m varies approximately as the cube root of H so that the "susceptibility" has no precise meaning; further, if $(\theta + \triangle\theta)$ is the temperature above which Weiss's law is obeyed, $\triangle\theta$ will be greater the greater the field. (As an example, for nickel, for which $\theta = 273 + 357$, for $H = 1{,}000$, $\triangle\theta \doteqdot 1{\cdot}6°$.) The transition from a ferro- to a para-magnetic state is therefore not abrupt, this being in agreement with Curie's results and later work.

An ordinary piece of iron can exist normally in an apparently stable unmagnetized state, and an outline will now be given of Weiss's reconciliation of this with the spontaneous magnetization view, and of his general theory of ferromagnetic phenomena. The theory is based on the attribution to the elementary constituent crystals of iron of properties analogous to those of pyrrhotite which he had previously studied. For the purpose of the theory, it is not necessary to consider the phenomena in detail; they may be accounted for in broad outline by supposing that an elementary pyrrhotite crystal contains one direction (OX) of "easy magnetization." In the absence of a field the magnetization may acquire its (quasi-) saturation value in the X direction; a field in the X direction will not increase the intensity; and if the field is reversed, the magnetization remains constant until the coercive value is passed, when the intensity changes in sign but not in magnitude. The hysteresis curves for fields in the X direction are simple rectangles. The saturation value in the OY direction is only acquired under a field of 7,300 gauss; in the OZ direction, about 150,000 gauss would be required. If N_1, N_2 and N_3 are the molecular field constants in the X, Y and Z directions $(N_1 - N_2)I = 7{,}300$, and $(N_1 - N_3)I = 150{,}000$.

Weiss supposes that ordinary iron is made up of crystals, or crystal aggregates, in each of which the magnetization corresponds to the spontaneous quasi-saturation value, in the direction of easy magnetization. If the crystals are orientated at random the resultant intensity will be zero. Consider the result of applying a gradually increasing field to crystals whose "magnetic axes" make an angle θ with the field. Let H_c be the coercive field required to reverse the direction of magnetization. Crystals with a resultant moment in the field direction will, to a first approximation, be unaffected; those with a moment in the opposite direction will suddenly reverse their direction of magnetization when $H \cos \theta = H_c$. Suppose there are n crystals per unit volume, with saturation moment μ_0, and let $n\mu_0 = I_0$. Then all the crystals with axes directed within a cone of semi-vertical angle θ to the field direction, where θ is given by $H \cos \theta = H_c$, will have a resultant moment in the field direction.

For a field H

$$I = \int_0^\theta \frac{n}{2\pi}\mu_0 \cos \theta . 2\pi \sin \theta d\theta$$

$$I = \frac{I_0}{2} \sin^2 \theta = \frac{I_0}{2}\left[1 - \left(\frac{H_c}{H}\right)^2\right] \quad . \quad . \quad . \quad . \quad (30)$$

This gives the maximum value that I will acquire under the influence of a field H (if not too large) and shows that, if the field is varied between + H and − H, somewhat angular hysteresis "loops" will be described; these give a first approximation to the loops actually observed; but by taking into account that the crystals may acquire also a (relatively small) magnetization at right angles to their main magnetic axes, and choosing suitable values for the constants H_c, $N_1 - N_2$, and $N_1 - N_3$, theoretical curves closely agreeing with the experimental are obtained, as shown by the two sets of Fig. 19.

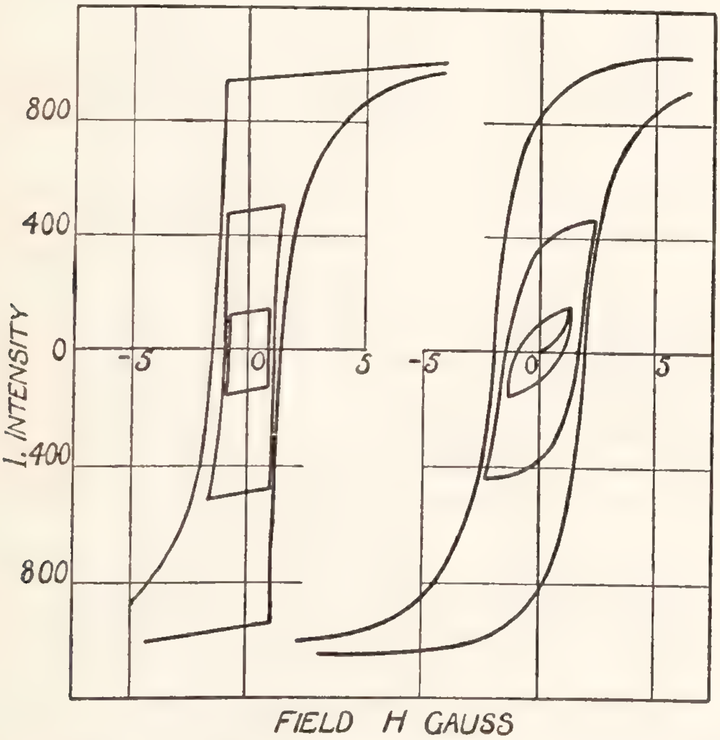

FIG. 19.—Hysteresis Curves: Theoretical (Weiss) and Experimental (Ewing).

In calculating the theoretical curves it was assumed that $I_{max} = 1{,}900$, $H_c = 1{\cdot}2$.

There are marked differences, but the general agreement is very striking—particularly as many of the divergencies can be accounted for by slight plausible modifications in the assumptions. It seems reasonable to suppose that the coercive force H_c, depending essentially on how each molecule is surrounded by its neighbours, may not be the same for each elementary crystal or crystal aggregate concerned; in particular, it will depend on the size of the aggregate, owing to demagnetizing fields.

As particular deductions from the theory, for a substance composed of similar elementary crystals of the simple type considered, the ordinate of the limiting cycle for $H = 0$ should be given by $I_{max}/2$. Now the mean residual intensity of magnetization is of the order of 1,000; and the maximum intensity observed, which is probably lower than the true quasi-saturation value, is 1,850. The curve for the limiting cycle should cut the H axis at $\sqrt{2}H_c$—this giving the coercivity; and in the theoretical curves the sudden beginning of the reversal of magnetization occurs for $H = H_c$.

The theory undoubtedly seems to be on the right lines; but there are many difficulties which remain to be discussed. In particular, as will be seen later, investigation of single iron crystals have shown that these do not possess marked directions of easy magnetization as is required by Weiss's theory, at least in its simple form.

4. Later Work. Difficulties and Problems

The work so far considered has been based almost entirely on classical conceptions. The quantum theory, to be taken up in the next chapter, sheds a good deal of light on many of the difficulties that arise; not by solving or "explaining" them, but by showing that they are simply special examples of difficulties of a much more general nature. A considerable number of attempts, independent of the quantum theory, have, however, been made to bring magnetic theory into closer harmony with experiment, mainly by modification of the Ewing-Langevin-Weiss ideas; some of these will be noticed in the present section; and a number of special problems and difficulties will be briefly discussed.

It seems impossible to doubt that the elementary magnets—whatever they may be—owe their magnetic properties to electrons rotating in orbits. Classically, such electrons should lose energy by radiation; but, as far as it is possible to draw definite conclusions from experiments, it may be stated that electrons can exist rotating in orbits in a stable state without radiating energy. It is therefore justifiable to treat such orbital electrons, to a large extent, simply as magnets.

The nature of the "carriers" is highly problematical. Considering paramagnetics, any change in magnetization involves essentially a change in orientation of electron orbits. The question then arises as to whether this involves also a change in orientation of a part of an atom, an atom as a whole (or an ion in solution), or a molecule as a whole. This cannot be adequately discussed until the quantum theory of atomic structure is considered; but it may be noted that while the rotation of molecules in a gas, or even of ions in solution, is readily conceivable—indeed the assumption that this occurs lies at the basis of Langevin's theory—the supposition that a similar rotation can occur in solids (as is, in effect, postulated in Weiss's theory) seems highly improbable. It must be borne in mind, moreover, that there must be some appropriate process—provided by intermolecular collisions in Langevin's theory—by which orientation may be brought about, for the field itself cannot directly orientate the electron orbits; this question as to the processes by which equilibrium is attained is connected with that as to how far the final equilibrium state will correspond to equipartition of energy among degrees of freedom; the quantum theory does provide a probably correct answer to this; but the processes involved remain obscure.

The electron theory of magnetism was considered by Voigt (1902) and J. J. Thomson (1903) before Langevin, and later by Kroo (1913) and others, with strikingly different results as to the possibilities of dia- and para-magnetic effects occurring. Voigt concluded that for a medium with an electronic structure such as was required to account for dispersion, the susceptibility should be zero, unless there were dissipative forces and collisions; the susceptibility might then be positive or negative according to the influence of the field on the effects of collisions, which, however, could not be calculated. Thomson also found, for a special type of atom model with rings of electrons, that the susceptibility should be zero, para- and dia-magnetic effects balancing each other. Kroo concluded that an electronic theory could only account for diamagnetism. Voigt, however, supposed the magnetic field to be established in an infinitesimal time, and Thomson also neglected the electric forces accompanying its growth, so that neither deduced the diamagnetic effect which necessarily results from the time for the establishment of the field being long compared with the orbital period of the electrons. The whole question has recently been very thoroughly treated by Fräulein van Leeuwen, who has shown that the results obtained for the final equilibrium state of magnetization depend on the distribution functions chosen and so, essentially, on the assumptions made as to what remains constant during the motion and collisions of the molecules. Kroo's conclusion that paramagnetism should not occur is due to his implicit assumption that during collisions the energy of the molecular systems remains constant, which is shown not to be justified ; the positive result of Langevin follows from the assumed constancy of the molecular magnetic moment.

There has been a considerable divergence of opinion as to whether free electrons should give rise to diamagnetism owing to the curvature of their paths under the influence of a magnetic field. According to Schrödinger (1912) and H. A. Wilson (1920) the effect should exist. Bohr and Lorentz, however, have shown that any diamagnetic effect arising from the electrons in the interior of a substance is precisely balanced out by those near the boundary ; and Leeuwen also concludes, from her general treatment, that the diamagnetic susceptibility, due to free electrons (assuming them to collide elastically with atoms), should be zero.

In a comprehensive series of papers Gans has attempted to improve the Langevin theory of para- and dia-magnetism. He bases his treatment on the assumption that substances are constituted of rigid axial "magnetons," capable of rotation, composed of a system of negative electrons within a positive sphere, the resultant charge and electric moment being zero. If the magnetons possess no figure axis, the substance will be diamagnetic. A paramagnetic susceptibility may or may not depend on the field strength and temperature according to the relative magnitudes of the principal moments of inertia of the magneton. By making suitable assumptions as to these, and also as to whether rotations about the principal axes are subject to thermal variation or not, Gans is able to account for a considerable number of "anomalous" experimental results. Gans's particular conception of the magneton is, however, so difficult to bring into relation with ordinary views of atomic structure, that it would probably not be fruitful to examine his theories in detail here. For a somewhat similar reason, Honda's theory (1914) will only be referred to. He assumes that substances may be composed of "magnetic molecules," which exert mutual forces on each other, which tend to prevent their lining up in the field direction. These magnetic molecules, which are subject to the usual laws governing thermal molecular motions, are made up of aggregates of actual molecules, so that their form and moment may vary with the temperature. Agreement with experiment can be obtained, but only by making an appropriate choice for theoretically indeterminate functions involved in the expressions arrived at.

As to ferromagnetics, Honda and Okubo (1916) extended Ewing's earlier treatment, considering the case of pivoted magnets distributed on a definite space lattice. The forms of hysteresis curves deduced are in close accord with experiment. All theories of this type, however, are subject to the inherent difficulty that if the elementary magnets are supposed to possess moments of magnitude such as are deduced from experiment, and to be separated by distances of the order of those between atoms in solids, the magnetic forces between them are insufficient to give rise to appreciable divergencies from the ordinary Langevin formulæ for feeble paramagnetics except at temperatures approaching absolute zero. This has been shown conclusively by Frivold (1921), who examined the whole question very completely, considering both linear and two-dimensional distributions of elementary magnets.

Gans has deduced a number of suggestive relations as to ferromagnetic behaviour, but his treatment again loses interest from the highly artificial character of the structures assumed; for ferromagnetics are supposed to be made up of ellipsoidal elementary complexes distributed with corresponding axes parallel on a space lattice, the complexes themselves containing a distribution of axial magnetons free to move, within the complex, like molecules in a gas.

It may be said that in essentials, and independently of the quantum theory, little has been added to the Langevin-Weiss views. The Weiss hypothesis of an intrinsic molecular field proportional to intensity certainly enables an enormous range of facts to be co-ordinated, but the nature of the field remains unknown. Before discussing this, it may be useful to consider briefly the relation between the views of Weiss and Ewing. The control on the elementary magnets in a ferro-magnetic may be regarded, according to Weiss, as arising from an effectively homogeneous field. On Ewing's view, the control arises from the heterogeneity which results from there being strong forces in the immediate neighbourhood of the poles of the elementary magnets which are regarded as possessing finite length. Considering a linear distribution of magnets, on Ewing's view, quasi-saturation would be approached once the magnets were deflected beyond their neutral equilibrium position; while according to Weiss, in relatively small fields, the magnet axes in an elementary crystal of the type assumed will point either in one or the opposite direction. Ewing does attempt to account for the mechanism involved; and although the theory is inadequate, and the mechanisms so far proposed do not work, it still seems premature to suppose that the whole idea is unwarranted.

Atomic structure and the electron orbit orientation possibilities which the quantum theory suggests must be discussed before any more definite conclusions may be drawn.

The molecular field hypothesis has been extraordinarily fruitful. Ferromagnetic phenomena may be interpreted on the basis of the laws for paramagnetics; both above and below the Curie point there is close accord with experiment. The properties of crystals may be simply coordinated. Magneto-thermal effects (notably a change in specific heat at the transition temperature) occur in accordance with prediction. Further, the experiments of Maurain on the behaviour of electrolytically deposited thin films of iron lend support to the view, while Oxley finds evidence for the existence of strong intrinsic fields in diamagnetics. The most striking feature of the field is the enormous magnitude it must possess, corresponding in magnetite for example, at ordinary temperatures, if interpreted as magnetic, to about $1{\cdot}7 \times 10^7$ gauss ($N \doteqdot 3{\cdot}3 \times 10^4$) in iron and nickel (with $N \doteqdot 3{\cdot}8 \times 10^3$, and $1{\cdot}3 \times 10^4$) to about 7×10^6 gauss.

The possible nature of the field has been discussed by Weiss (1914). The moment of the iron atom corresponds roughly to a value of $1{\cdot}8 \times 10^{-20}$; making the unplausible assumption that the "magnet" has a finite length of atomic dimensions—2×10^{-8} cm.—it follows that a field of 6×10^7 gauss would only be produced very close to the "poles," namely at a distance r $\left(\text{given by } \dfrac{1{\cdot}8 \times 10^{-20}}{2 \times 10^{-8} r^2} = 7 \times 10^6\right)$ equal to about $3{\cdot}6 \times 10^{-10}$ cm. This suggests that, even making favourable artificial assumptions, the field cannot be supposed to be magnetic. For an electron orbit the maximum field is at the centre; and for an electron describing the normal orbit in the hydrogen atom the field at the centre is of the order of 10^5 gauss; again, the magnitude is much less than that required.

It seems therefore highly improbable that the field can be interpreted as being of magnetic origin. From a study of the variation in magnitude of the molecular field constant with the composition of various ferromagnetic alloys, Weiss is able, however, to draw some interesting conclusions as to the variation of the law of force between the elementary magnets. Nickel-cobalt alloys show a linear variation of N with composition (from 14,000 for 100 per cent. Ni to 8,600 for 100 per cent. Co); Weiss supposes that such a linear variation would occur, if there were no disturbing factors, if one of the metals of a binary alloy was para- or dia-magnetic. This would give $N = N_1\varrho$, ϱ being the density of the ferromagnetic constituent; if $I_s\left(=\frac{I}{\varrho}\right)$ is the specific intensity of magnetization, and H_i the molecular field,

$$H_i = N_1\varrho I = N_1 I_s \varrho^2$$

Now if r is the distance between the elementary magnets $\varrho \propto \frac{1}{r^3}$, so that

$$H_i = k \times \frac{1}{r^6}$$

This at once suggests—as may easily be shown with more rigour—that the force from the magnetic molecule which gives rise to the molecular field varies inversely as the sixth power of the distance. Weiss obtains confirmatory evidence for such a law of force from Maurain's experiments, and the parts of his results which are relevant may be briefly described. Maurain found that when iron was deposited electrolytically in a magnetic field (the field being in the plane of the film) the magnetic moment increased proportionally to the thickness when this exceeded some 80 $\mu\mu$. If the direction of the field was then changed, provided it did not exceed the coercive field (actually an inverse field of 1·65 gauss was employed), the magnetic moment of the film on further deposition continued to increase in the initial direction—the effect of the molecular field being greater than that of the applied field. Intermediate films of neutral metals were then deposited, and it was found that with a thickness of 38 $\mu\mu$ of copper or gold, the two fields balanced, subsequent deposition of iron being accompanied by a slight increase in magnetic moment in the applied field direction. Knowing the magnitude of the molecular field in the interior of the substance (7×10^6 gauss) and taking its value at a boundary to be half this, and taking $2{\cdot}2 \times 10^{-8}$ cm. as the molecular diameter, if the force due to the molecular field falls off as $1/d^m$, d being the distance from the surface, it follows that

$$\left(\frac{380}{1{\cdot}1}\right)^m = \frac{3{\cdot}5 \times 10^6}{1{\cdot}65}$$

so that $m = 2{\cdot}5$. If the law of force between the elementary magnets varies as $1/r^n$, it may be deduced, remembering that the $m = 2{\cdot}5$ applies to distance from a bounding surface, that $n = 3 + 2{\cdot}5 = 5{\cdot}5$. The agreement between the results obtained by two quite different methods confirms the belief that Maurain's "magnetizing action of contact" and "molecular field phenomena" have the same origin; and it seems quite certain, in spite of the assumptions involved in each argument, that the force between molecules to which the intrinsic field is due falls off much more rapidly than the third power of the distance.

This point is of importance in connection with the suggestion that the field might be of an electric nature, arising from the molecules being electric dipoles as well as elementary magnets, the magnetic moment having an electric moment associated with it; this might give effects of the right order of magnitude; but the force between the molecules should follow an inverse cube law. Moreover, it should always give rise to a positive molecular field, while negative molecular fields frequently occur.

It may be noted that it is possible to write $-\partial U/\partial I$ for the molecular field instead of H_i, U being the energy of the substance per unit volume; this formulation is independent of special hypotheses; but actually it only leaves the central question to be stated in a different form. The reason for the change in internal energy with intensity of magnetization has still to be sought, and in particular why the relative change is so much greater in some substances than others.

This section—and chapter—must then be concluded, with the nature of the molecular field as unknown, and also the nature of the carriers of the elementary magnets undetermined. These form two of the outstanding problems of magnetic theory.

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CHAPTER V

THE QUANTUM THEORY

1. The Origin and Development of the Quantum Theory

THE quantum theory as a whole has been so frequently and admirably presented that a general familiarity with it will be assumed. It seems desirable, however, in the present section, to recall as briefly as possible some of the main features in its development, partly for the sake of completeness, but mainly in order that the wider significance of particular magnetic applications, and the basis for them, may be more clearly realized.

The theory arose in the attempt to overcome classical difficulties in connection with temperature radiation. If matter is in equilibrium with the surrounding radiation field in an isothermal enclosure, simple thermodynamic reasoning shows that

$$\varepsilon_\nu / a_\nu = \kappa_\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

ε_ν and a_ν being the emission and absorption coefficients and κ_ν the specific intensity of the equilibrium temperature radiation. The equation implies that the radiation absorbed per unit time must be equal to that emitted. Now κ_ν, a function of ν and the temperature T, is known experimentally to be independent of the nature of the material substance. The relation (1) must therefore hold not only for every particular frequency (or small range of frequencies), but for every particular type of absorbing and emitting mechanism. Moreover, to every particular absorption process there must be a corresponding exactly inverse process of emission. These more specific conditions are necessary in order that equilibrium may be maintained not only in the distribution of the energy as a whole between the matter and the radiation, but also in the distribution, as regards relative numbers, of the different kinds of individual material agents present (molecules, atoms, free electrons), and for each kind among the different possible energy states.

By further very general thermodynamical reasoning it is possible to deduce Wien's law, that

$$\kappa_\nu = \frac{\nu^3}{c^2} f\left(\frac{\nu}{\mathrm{T}}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

but the form of $f\left(\frac{\nu}{\mathrm{T}}\right)$ cannot be determined without making specific hypotheses as to the processes of emission and absorption. For different mechanisms, however, it is possible to calculate classically ε_ν and a_ν, and hence, from (1), to deduce κ_ν. For "resonators," free electrons, and electrons in orbits, the result is the same, namely

$$\kappa_\nu = \frac{\nu^2}{c^2} k\mathrm{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

k being Boltzmann's constant. This result, however, follows at once by applying the equipartition theory to the stationary vibrations of the æther (or occurring in the free space) in an isothermal enclosure. The number of such stationary vibrations per unit volume may be shown to be $\mathrm{C}\lambda^{-4}d\lambda$, where C, for transverse light waves, is equal to 8π. If there is equipartition of kinetic energy among degrees of freedom, each possessing the average amount $\frac{1}{2}k\mathrm{T}$, as in the usual gas theory, remembering that for vibrational degrees of freedom the potential energy is equal to the kinetic, for the energy in a range $d\lambda$ it follows that

$$\mathrm{E}_\lambda d\lambda = 8\pi k\mathrm{T}\lambda^{-4}d\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

or

$$\mathrm{E}_\nu d\nu = \frac{8\pi}{c}\frac{\nu^2}{c^2} k\mathrm{T} d\nu$$

—the same result as in (3), since $\mathrm{E}_\nu = \frac{8\pi}{c}\kappa_\nu$.

The result (3) or (4), indicating that the radiational energy will be concentrated in the shortest wave-lengths (and also, since the limiting wave-length—if there is a limit—must be very short, that practically all the energy should be found in the radiational field and not in the matter), is in complete disaccord with experiment, which shows that within the limits of error

$$\kappa_\nu = \frac{\nu^2}{c^2} k\mathrm{T} \times \left\{ \frac{h\nu}{k\mathrm{T}} \Big/ \left(e^{\frac{h\nu}{k\mathrm{T}}} - 1 \right) \right\} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

or

$$\mathrm{E}_\lambda = 8\pi k\mathrm{T}\lambda^{-4} \times \left\{ \frac{h\nu}{k\mathrm{T}} \Big/ \left(e^{\frac{h\nu}{k\mathrm{T}}} - 1 \right) \right\} \quad . \quad . \quad . \quad (5.1)$$

where h is Planck's constant, equal to $6{\cdot}55 \times 10^{-27}$ erg × sec. This is the expression obtained by Planck (1900), who considered the special case of a simple harmonic resonator. The essential assumption involved in his treatment (though expressed differently by him) is that energy interchanges between matter and radiation do not take place continuously, but only by discrete quanta ε, such that $\varepsilon = h\nu$.

The simplest method of deriving (5.1) is probably that of Jeans (1910), who considers the stationary "ætherial" vibrations. It is supposed that the vibrations of wave-length λ, corresponding to a frequency ν, can only possess energy in multiples of $h\nu$. Then, if N is the total number of vibrations, and M possess zero energy, by an extension of kinetic theory from continuous to discontinuous states, the numbers possessing energies $h\nu$, $2h\nu$ . . . will be $\mathrm{M}e^{-\frac{h\nu}{k\mathrm{T}}}$, $\mathrm{M}e^{-\frac{2h\nu}{k\mathrm{T}}}$ . . . The general validity of this extension has been examined by Brillouin (1921), who concludes that it is justifiable. Essentially it is justified by the results. For the total number of vibrations N, the total energy $\mathrm{E_T}$, and the mean energy per vibration $\bar{\mathrm{E}}$

$$\mathrm{N} = \mathrm{M}(1 + e^{-\frac{h\nu}{k\mathrm{T}}} + e^{-\frac{2h\nu}{k\mathrm{T}}} + \ldots) = \mathrm{M}/(1 - e^{-\frac{h\nu}{k\mathrm{T}}}) \quad . \quad . \quad . \; (6)$$

$$\mathrm{E_T} = \mathrm{M}h\nu(e^{-\frac{h\nu}{k\mathrm{T}}} + 2e^{-\frac{2h\nu}{k\mathrm{T}}} + \ldots) = \mathrm{M}h\nu e^{-\frac{h\nu}{k\mathrm{T}}}/(1 - e^{-\frac{h\nu}{k\mathrm{T}}})^2 \quad . \; (7)$$

$$\bar{\mathrm{E}} = \mathrm{E_T}/\mathrm{N} = h\nu/(e^{\frac{h\nu}{k\mathrm{T}}} - 1) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; (8)$$

(8) gives the mean energy for each vibration which must be substituted for (kT) in (4), bringing the result into harmony with the experimentally verified formula (5.1).

Einstein (1917) has also shown that (5.1) can be derived for a Bohr atom which can exist in different energy states $\mathrm{E_1}$, $\mathrm{E_2}$ . . ., and such that transitions between these states are accompanied by absorption or emission of radiation of frequency ν given by $\frac{|\mathrm{E_1} - \mathrm{E_2}|}{h}$.

In 1905, Einstein applied the quantum theory to the photoelectric effect. When radiation falls on matter, if a limiting frequency is exceeded, photoelectrons are emitted whose velocity is independent of the intensity of the radiation, and depends only on its frequency. Einstein's photoelectric equation

$$\tfrac{1}{2}mv^2 = h\nu - w \quad . \; . \; . \; . \; . \; . \; . \; . \; (9)$$

implies that a whole quantum is absorbed, the observed energy of the electron being equal to the energy of this, less that required to remove it from the atom and to carry it beyond the boundary of the material. At the same time Einstein put forward the light-dart hypothesis, according to which radiational energy is not only emitted or absorbed in quanta, but also exists in free space in the form of discrete localized bundles of energy or quants. While this is not a necessary consequence of (9), later work has shown that, if there is conservation of energy and momentum in individual absorption and emission processes, there seems no escape from the conclusion that radiational energy is propagated by means of linearly directed spatially localized quants. This is supported by the recent work confirming the Compton-Debye quantum theory of scattering. Up to the present, however, it has not proved possible to explain interference effects in terms of quants.

The inadequacy of classical theory was very apparent in connection with the specific heat of solids. If three vibrational degrees of freedom could be attributed to each atom in a solid, the atomic heat should be equal to 3R(5·95) in accordance with Dulong and Petit's law. While this was approximately true at moderately high temperatures, at low temperatures there were wide discrepancies. Einstein (1905), by attributing to the atoms a mean vibrational energy given by (8) in place of kT, was able to account qualitatively for the results, in particular for the falling off of the specific heat at low temperatures. His treatment was semi-empirically extended by Nernst and Lindemann. The most successful attack on the problem, however, is that of Debye (1912) who focusses attention not on the individual atoms, but on the solid as a whole, and considers the thermal motions as equivalent to a system of stationary elastic solid vibrations. To each of these vibrations is assigned the quantum theory mean energy (8); and an upper limit for the frequency is found by supposing the total number of vibrations is equal to the number of vibrational degrees of freedom, three to each atom. This leads to the result that the specific heat at any temperature T is given by $f\left(\frac{\theta}{\mathrm{T}}\right)$ where the function is the same for all substances, θ being characteristic for each. The results are in close agreement with experiment even at very low temperatures. Born and Karman (1913) modified Debye's treatment by taking into account the arrangement of atoms on a space lattice.

The specific heat of gases presents analogous difficulties. The central problem is to determine what modes of rotation of the molecule and of vibrations of its constituent atoms are possible, whether these are subject to thermal variations, and what is the appropriate mean energy to be assigned to each. Exactly what is the appropriate formulation of quantum conditions for the fixation of stationary states in atoms is still a matter of uncertainty ; and the treatment has as yet only been tentatively extended to molecules. Just as line spectra have proved a key to atomic structure, however, so are band spectra enabling the structure of molecules to be elucidated ; and the study of band spectra in conjunction with molecular specific heats will undoubtedly be extremely fruitful. At present the experimentally observed gaseous specific heats enable conclusions to be drawn as to whether rotations and oscillations occur to an appreciable extent ; but more precise theories so far advanced are necessarily very inadequate.

An epoch in the history of the quantum theory is marked by the publication in July, 1913, of the first of Bohr's famous papers, *On the Constitution of Atoms and Molecules.* The simplest case of an atom of the Rutherford type was there considered with a single negative electron revolving round a massive positive nucleus. The relatively simple treatment has been refined and extended by Bohr himself, Sommerfield and many others, and the theory will be briefly sketched in the light of this later work.

It has already been mentioned that for electrons rotating in orbits about a nucleus there can be no continuous loss of energy by radiation as the classical theory would predict ; there must be possible "stationary" (non-radiating) states of the electrons. Bohr extended the original quantum theory of Planck to the fixation of these stationary states, and the first fundamental postulate by which this is done may be expressed, if u is the degree of periodicity of the system, by u equations of the form

$$J_u = \tau_u h \qquad \qquad (10)$$

Here the J_u are the conjugated momenta of certain uniformizing variables defining the motion of the system, h is Planck's constant, and τ_u is a whole number.

For multiply periodic systems, when the variables are separable, (10) becomes

$$\oint p_u dq_u = \tau_u h \qquad \qquad (10.1)$$

p_u and q_u being the conjugated momentum and space co-ordinates, and the integral being taken over a complete period. The content of these equations may be seen by considering the simple case of an electron describing a circular orbit. Taking as co-ordinate, $\dot{\phi}$ being the angular velocity, (10.1) becomes

$$\oint mr^2\dot{\phi}d\phi = \tau h \quad . \; . \; . \; . \; . \; . \quad (10.2)$$

$$mr^2\dot{\phi} = \tau\frac{h}{2\pi} \quad . \; . \; . \; . \; . \; . \quad (10.3)$$

Essentially, in this case, the postulate asserts that the angular momentum can only assume certain discrete values.

Exchange of energy between the atom and the radiation field only occurs through a transition between two stationary states. The second postulate asserts that such a process results in the emission of harmonic waves whose frequency is given by

$$h\nu = E_1 - E_2 \quad . \; . \; . \; . \; . \; . \quad (11)$$

E_1 and E_2 being the initial and final energies of the system.

The nature of the transition process is left quite undefined, and this constitutes one of the main shortcomings of the theory. Fortunately the problem does not seem beyond the range of experimental and theoretical attack, though so far it remains very obscure. It will be seen later that the transition problems are closely related to those connected with magnetic orientation.

On the basis of the two postulates, the behaviour, in their spectral and energy relations, of atoms consisting of a nucleus and one electron can be described in a wonderfully complete and satisfying manner. For atoms containing more than one electron, there are difficulties; these are partly mathematical, but partly also arise because classical electrodynamics, even when radiation is neglected, is inadequate to describe completely the interaction of the electrons. It is possible, however, on the basis of the postulates, to interpret the atomic spectra, which assume significance in enabling the energy associated with different possible stationary states to be calculated. Before proceeding to the general problem of atomic structure, however, the results obtained as to possible orbital forms, and the corresponding energies for mono-electronic atomic systems, will be stated. Some numerical data are also collected to give an idea of the magnitudes involved, and for future reference.

The stationary states for an electron in central motion about a nucleus of charge Ne may be characterized by two quantum numbers n and k; n, the principal quantum number, determining to a first approximation the energy of the atom and the major axis of the elliptical orbit, and k, the azimuthal quantum number, which determines the angular momentum of the electron about the nucleus, and fixes the eccentricity of the (rotating) orbit.

Then for possible energy values for the stationary states, approximately

$$E_n = -\frac{2\pi^2e^4m}{h^2}\frac{N^2}{n^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

or, taking into account the relativity change of mass with velocity

$$E_{nk} = -\frac{2\pi^2e^4m}{h^2}\frac{N^2}{n^2}\left[1 + \frac{4\pi^2e^4}{h^2c^2}\frac{N^2}{n}\left(\frac{1}{k} - \frac{3}{4n}\right)\right] \quad . \quad (12.1)$$

From (11), using (12)

$$\nu = \frac{c}{\lambda} = \frac{2\pi^2e^4mN^2}{h^3}\left(\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right) \quad . \quad . \quad . \quad . \quad (13)$$

where ν is the frequency of the radiation emitted.

Expressed in wave numbers ν',

$$\nu' = \frac{1}{\lambda} = \frac{2\pi^2e^4mN^2}{h^3c}\left(\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right) \quad . \quad . \quad . \quad (13.1)$$

$$= RN^2\left(\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right) \quad . \quad . \quad . \quad . \quad (13.2)$$

The spectroscopic value for R is $1\cdot097 \times 10^5$; that calculated from (13.1), using the values $\frac{e}{mc} = 1\cdot767 \times 10^7$, $e = 4\cdot774 \times 10^{-10}$, $h = 6\cdot545 \times 10^{-27}$, is $1\cdot098 \times 10^5$. Thus the wave-number term values are given by

$$\nu_T{}' = 1\cdot097 \times 10^5\frac{N^2}{n^2} \quad . \quad . \quad . \quad . \quad . \quad (14)$$

or, with the correcting factor of (12.1),

$$\nu_T{}' = 1\cdot097 \times 10^5\frac{N^2}{n^2}\left[1 + 5\cdot32 \times 10^{-5}\frac{N^2}{n}\left(\frac{1}{k} - \frac{3}{4n}\right)\right] \quad (14.1)$$

For the negative energies W_n of the atom, from (12)

$$\left.\begin{aligned} W_n &= -E_n = Rhc\frac{N^2}{n^2} \\ &= 2\cdot153 \times 10^{-11}\frac{N^2}{n^2} \text{ ergs} \\ &= 13\cdot53\ \frac{N^2}{n^2} \text{ equivalent volts} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (15)$$

equivalent volts being the number of volts through which an electron must fall to acquire the equivalent energy. It may be convenient to note here various other energy magnitudes expressed in similar form. For the energy of a quantum

$$h\nu = \frac{12{\cdot}34 \times 10^3}{\lambda} \text{ equivalent volts} \quad . \quad . \quad (16)$$

λ being expressed in Angstrom units. Quanta for visible radiation have energies ranging from about 1·5 to 3 volts.

The molecular translational energy is equal to $\frac{3}{2}k\mathrm{T}$. Taking R, the gas constant per gram molecule, expressed in ergs, as $8{\cdot}315 \times 10^7$,

$$\begin{aligned} k\mathrm{T} &= 1{\cdot}37 \times 10^{-16}\ \mathrm{T} \text{ ergs} \\ &= 8{\cdot}63 \times 10^{-5}\ \mathrm{T} \text{ equivalent volts} \quad . \quad . \quad (17) \end{aligned}$$

This is quite small, the whole mean translational energy of a molecule even at 2,000° absolute only being "equivalent" to about $\frac{1}{4}$ volt.

The following expressions give the values for the major and minor axes ($2a$ and $2b$), the latus rectum ($2p$) and the eccentricity of the elliptic orbits.

$$\left.\begin{aligned} 2a &= \frac{n^2}{\mathrm{N}} \frac{h^2}{2\pi^2 e^2 m} \\ &= 1{\cdot}064 \times 10^{-8} \frac{n^2}{\mathrm{N}} \text{cm.} \\ a &= \frac{n^2}{\mathrm{N}} a_{\mathrm{H}} \text{ where } a_{\mathrm{H}} = {\cdot}532 \times 10^{-8} \text{ cm.} \end{aligned}\right\} \quad . \quad (18)$$

a_{H} being the radius of the normal (1, 1) hydrogen orbit.

$$\left.\begin{aligned} 2p &= \frac{k^2}{\mathrm{N}} \frac{h^2}{2\pi^2 e^2 m} = \frac{k^2}{n^2} 2a \\ b &= \frac{k}{n} a = \frac{nk}{\mathrm{N}} a_{\mathrm{H}} \\ 1 - \varepsilon^2 &= \frac{k^2}{n^2} \end{aligned}\right\} \quad . \quad (19)$$

The periodic time τ depends on n:

$$\tau = \frac{h^3}{4\pi^2 m e^4} \cdot \frac{n^3}{\mathrm{N}^2} = \frac{1}{2\mathrm{R}c} \frac{n^3}{\mathrm{N}^2} \quad . \quad . \quad . \quad (20)$$

while the mean areal velocity $\bar{\mathrm{A}}$ depends only on k:

$$\bar{\mathrm{A}} = \frac{\pi a b}{\tau} = \frac{hk}{4\pi m} \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

This, of course, at once follows from (10.1), putting $q = \phi$, and $p_\phi = mr^2\dot{\phi}$ so that $\oint mr^2\dot{\phi}d\phi = kh$,

giving
$$r^2\dot{\phi} = 2\bar{\mathrm{A}} = \frac{kh}{2\pi m} \quad . \quad . \quad . \quad . \quad . \quad (21.1)$$

In concluding this section two guiding principles which have been of the utmost value in the formal development of the quantum theory should be referred to—the Correspondence Principle of Bohr and the Principle of the Adiabatic Invariance of Quantum Integrals, developed largely by Einstein, Ehrenfest and Burgers.

According to the adiabatic-invariance principle, functions such as J or $\oint pdq$ which occur in the quantum equations (10) and (10.1) must be such that they remain unchanged in value when the parameters specifying the strength of an external field of force are gradually changed. The number of possible functions satisfying this condition is very restricted. The principle is of particular value in considering limiting cases when the external field is reduced to zero.

The correspondence principle may be most easily approached by considering the simple case of the hydrogen atom, when n is large; then, from (13),

$$\nu = \mathrm{R}c\frac{2}{n^3}(n_2 - n_1) \quad . \quad . \quad . \quad . \quad . \quad (22)$$

so that, if f is the frequency of the electron in its orbit, using (20),

$$\nu = (n_2 - n_1)f \quad . \quad . \quad . \quad . \quad . \quad (22.1)$$

The frequencies emitted are thus those which would be expected on the classical theory. Bohr's principle asserts that a " correspondence " may be supposed to persist for small quantum numbers; and classical principles may then be applied to determine the nature, as regards polarization, of the radiation emitted for particular types of transitions, to " select " which transitions may occur, and also to estimate the intensities of spectral lines.

It must be noticed that the principle does not help to solve classical-quantum difficulties. It enables results to be calculated which are in rough agreement with experiment; but at present no satisfying explanation can be given as to why it should " work " in this way.

2. Atomic Structure

For full details of Bohr's Theory of the Constitution of Atoms, reference must be made to his original papers, and to the many expositions which have since appeared. Here the guiding principles and conclusions will be recalled, and the modifications to the original scheme suggested by later work, some of which seem suggestive in connection with magnetism, will be briefly discussed.

Bohr supposes atoms to be built up by a process of successive binding of electrons by a nucleus, and from a consideration of the X-ray and optical spectra (of neutral and ionized atoms) he is able to draw conclusions as to the quantum-group distribution and the energy relations of electrons. As the atomic number increases a sequence of properties is suggested which is in remarkable accord with that summarized in the periodic table. The chemical behaviour of the atoms provides a second source of information, particularly with regard to the more loosely bound electrons. The state of an atom corresponding to the orbital motion of a particular electron (whose transitions give rise to the spectral lines) can be characterized in general by three quantum numbers, n and k, already considered, and j, the inner quantum number, which is connected with the spatial orientation of the orbit, but whose precise physical significance may for the present be left indeterminate. The primary division of electrons in the atom is into groups occupying levels characterized by different values of n. ($n = 1, 2, 3 \ldots$ for K, L, M . . . levels.) These levels are subdivided according to different values of k ($k = 1, 2 \ldots n$) and j (j may most conveniently, for present purposes, be taken to assume the values k and $k - 1$).

A specification of the structure of the atom, then, involves a knowledge of the energy corresponding to the n, k, j levels (that is, the energy required to remove an n, k, j electron from the atom) and the number of electrons in these levels. The first part of the problem can largely be solved by an investigation of the spectra in virtue of the second postulate; the second involves consideration of the atom-building process. Definite groups of lines in spectra, for example, require the presence of definite groups of electrons, so that from the points of appearance of these lines and their subsequent changes, the points of appearance and mode of development of the corresponding electron groups can to a certain extent be deduced. The final distribution of electrons in completed atoms suggested by Bohr was, however, based on somewhat arbitrary symmetry considerations.

Bohr's scheme may conveniently be discussed with reference to Tables III and IV. Table III, worthy of its frequent reproduction, gives a survey of the periodic system in the suggestive form used by Bohr, originally proposed by Julius Thomson.

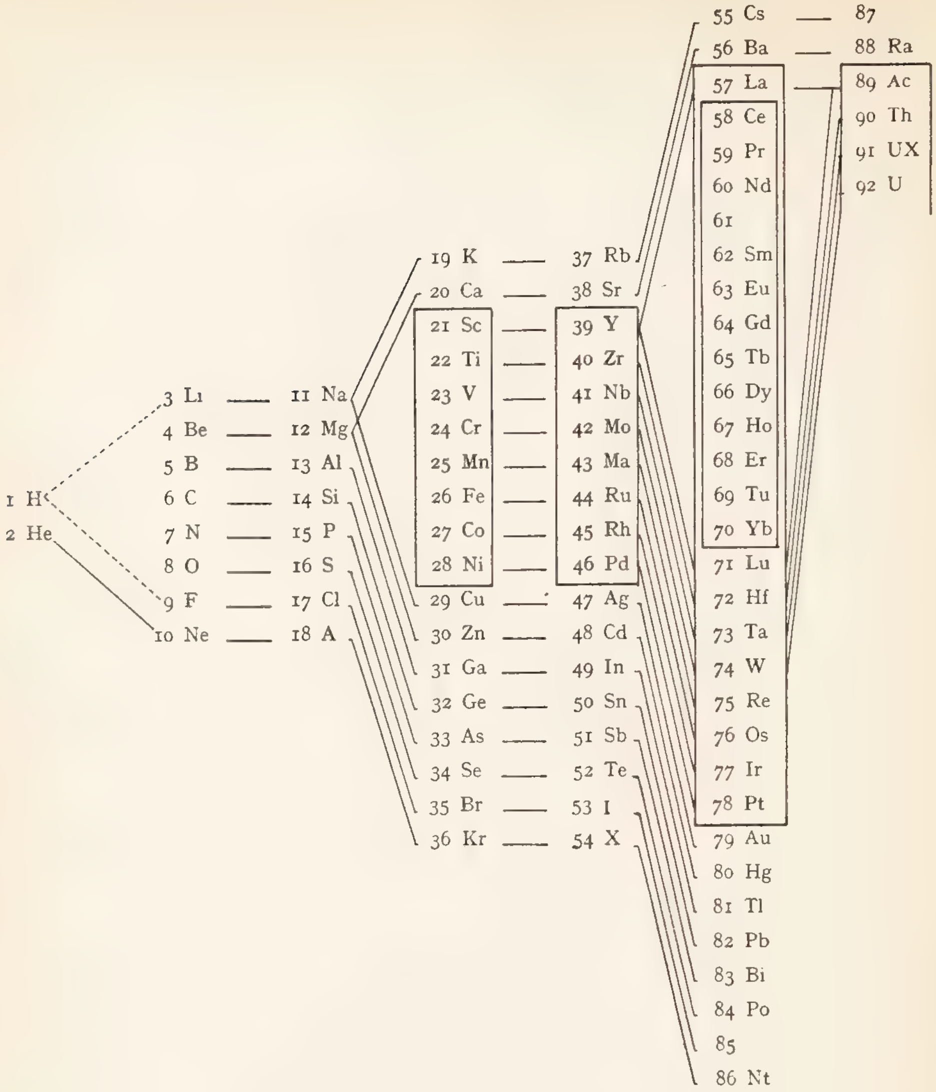

TABLE III.—THE PERIODIC SYSTEM.

Table IV gives the constitutions proposed by Bohr for the inert gases, which may be regarded as having "completed" configurations. (In this there are analogies with the more formal and empirical Lewis-Langmuir theories.)

Bohr considers only the (n, k) subdivision of levels. H and He have 1 and 2 electrons in the (1, 1) level, the K group then being completed. In passing from Li to Ne electrons are added to the (2, 1) and (2, 2) levels until the L group is complete with 8 electrons at Ne. Other groups with analogous properties (Table III) owe their similarity to the fact that outer levels for which $k = 1$ and 2 are being filled up in a precisely similar manner, though n increases for each group—

Element.	Atomic Number.	Sub-levels (*n*, *k*).														
		K	L		M			N				O			P	
		1	2	2	3	3	3	4	4	4	4	5	5	5	6	6
		1	1	2	1	2	3	1	2	3	4	1	2	3	1	2
He	2	2														
Ne	10	2	4	4												
A	18	2	4	4	(4	4)—										
Kr	36	2	4	4	(6	6	↓ 6)	(4	4)—							
X	54	2	4	4	6	6	6	(6	6	↓ 6)……		(4	4)—			
Nt	86	2	4	4	6	6	6	(8	8	8	↓ 8)	(6	6	↓ 6)	4	4

TABLE IV.—DISTRIBUTION OF ELECTRONS IN ATOMS, ACCORDING TO BOHR.

Li — Ne ($n = 2$), Na — A ($n = 3$), Cu — Kr ($n = 4$), Ag — X ($n = 5$), Au — Nt ($n = 6$).

Although the total quantum number may be large, the (negative) energy of the orbits will be much greater than that of corresponding n hydrogen atom orbits; for, owing to the strong ellipticity, the orbits will penetrate the electronic core, and for part of their path the electrons will move under the influence of a central positive charge which may be much greater than unity. It is unnecessary to enter into detail regarding the correspondence between the energies of the orbits deduced from the spectra and the chemical properties of the elements.

The addition of electrons and the consequent development of chemical properties does not always proceed in the simple manner so far described; and it is perhaps one of the main triumphs of the Bohr theory that it provides a straightforward and satisfying explanation of the occurrence and properties of "transition" groups of elements. (These are enclosed in frames in Table III.) The sequence of elements from A (18) to Cu (29) will be considered in illustration. In A the K and L levels are filled with 2 and 8 electrons, and there are 8 electrons in the (3, 1) and (3, 2) orbits. The M levels are not completely filled. In spite of this, in K, the 19th electron does not go into a (3, 3) level but into a (4, 1), because, owing to its penetration, a (4, 1) electron will be more closely bound than a (3, 3). Similarly in Ca, the 20th electron also enters a (4, 1) level. With increase in nuclear charge, however, the negative energy and the corresponding "firmness of binding" of a (3, 3) electron increases more rapidly than that of a (4, 1); and in Sc (21) it appears, from an examination of the spectra, that the 19th electron would enter a (3, 3) orbit. In proceeding from Sc (21) to Ni (28) the main development occurs in the underlying M group. From Cu (29) to Kr (36) normal development is resumed; and from this it may be concluded that the first 28 electrons in copper constitute a "completed" configuration with 2, 8 and 18 electrons in the K, L and M levels. The exact manner in which the development occurs, and the precise constitution of the elements, cannot at present be followed in detail; but the whole process may be described as a "reorganization" of the M group. This "reorganization" occurring from Sc to Ni is indicated by the first continuous arrow in Table IV. Similar reorganizations of the N ($n = 4$) and O ($n = 5$) groups occur in passing from Y (39) to Pd (46) and from Lu (71) to Pt (78), which are also indicated. The rare-earth group corresponds to a different type of reorganization, in which a $k = 4$ level is filled up, the number of electrons in the N group as a whole increasing from 18 to 32. This is indicated by the dotted arrow in Table IV.

The main shortcomings of the original Bohr scheme are that all the sub-levels known to exist are not separately considered; and that the final distribution proposed (Table IV) is based on somewhat arbitrary arguments as to symmetry requirements. Now the experiments on X-ray absorption, and on secondary electrons emitted by X-rays, show quite definitely that there are 1K, 3L, 5M and probably 7N levels; these are also required to co-ordinate the emission spectra lines. Moreover, the X-ray spectra show complete analogy with the optical doublet spectra of the alkalis, so that it becomes possible to assign to the levels as appropriate k and j values those which co-ordinate the optical spectra. These values are shown in Table V, which gives the modification of the Bohr scheme suggested as to electron distribution when all the levels are taken into account.

The 224 distribution of the L electrons was proposed by de Broglie and Dauvillier; but for the other groups they assumed numbers of levels (6M, 10N . . .) which are not in harmony with the spectral data. The distribution of Table V was first suggested as a whole by Main-Smith, chiefly on the basis of chemical arguments; and it was later put forward independently by Stoner. The general arguments for the validity of the

Element	Atomic Number	Level (n)	Sub-level (k, j)						
			I	II	III	IV	V	VI	VII
			1, 1	2, 1	2, 2	3, 2	3, 3	4, 3	4, 4
He	2	K (1)	2						
Ne	10	L (2)	2	2	4				
A	18	M (3)	2	2	4	(4	6)		
Kr	36	N (4)	2	2	4	(4	6)	(6	8)
Xe	54	O (5)	2	2	4	(4	6)		
Nt	86	P (6)	2	2	4				

TABLE V.—DISTRIBUTION OF ELECTRONS ACCORDING TO THE MODIFIED BOHR SCHEME.

(The distribution of electrons in the atoms is given by the part of the table above and to the left of the thick lines.)

scheme and the experimental evidence supporting it may be briefly summarized.

It has been mentioned that the X-ray spectra are completely analogous to the alkali metal doublet spectra (or more generally to doublet spectra of atoms neutral or ionized having one series electron external to a "completed" core). Thus the L_{I}, L_{II} and L_{III} levels correspond to $2s$, $2p_1$, and $2p_2$ optical levels, the M to $3s$, $3p_1$, $3p_2$, $3d_2$ and $3d_3$. The "relativity" formula which applies to the L_{II}, L_{III} separation also gives very closely the observed $2p_1$, $2p_2$ optical separation (as shown in particular by the work of Millikan and Bowen on the spectra of multiply ionized atoms), although the relativity explanation, as will be discussed more fully in connection with the Zeeman effect, is probably untenable.

For the optical doublet levels, corresponding to a given nkj, the number of possible sub-levels is equal to $2j$. In the absence of an external magnetic field the sub-levels have the same energy ; but when a weak field is applied, it may be deduced from the splitting of the spectral lines that each *nkj* level splits up into $2j$ sub-levels, separated at intervals proportional to the magnetic field. These sub-levels correspond to distinct possible orbits for the electron, differing, with the atoms as wholes, in their orientation. Each state may be characterized by a distinct magnetic quantum number m, which is independent of the strength of the field. Even when the field is indefinitely reduced, there will still be the same number of distinct possible states. This suggests that in the upbuilding of atoms, electrons may be added in each *nkj* group until there is one electron corresponding to each possible distinct state ; so that the numbers in completed configurations will be those given in Table V.

The adoption of the scheme which applies to optical doublet systems for " completed " atomic configurations is not purely arbitrary. In a doublet atom (such as sodium) there is a completed core, and the series electron can occupy any of the levels constituting the next group ; energy changes involve transitions of this one electron from any of the possible levels. In a completed configuration all the possible levels are occupied, and energy changes involve transitions of any of the electrons. It would be expected that the appropriate j (and m) values would be the same. Pauli has pointed out that this is a special case of a " reciprocity law," that to every arrangement of electrons there is a conjugated arrangement, the j values for each being the same, and the sum of the electrons in the two arrangements being equal to that in the completed group or sub-group. Thus, an L group ($n = 2$) with 1 or 2 electrons is " conjugate " to one with 7 or 6. The possible states, as specified by the quantum numbers, will be the same ; though the corresponding states for the two arrangements will not in general have the same relative probabilities owing to differences in the energies of the levels concerned. As a further example of the application of the principle, it may be mentioned that Wentzel has advanced the view that X-ray " spark " spectra (corresponding to the loss of two electrons from a completed configuration) are to be co-ordinated as a triplet system, like the spectra arising from atoms with two electrons in addition to a completed configuration.

It should be emphasized that the *kj* classification adopted in Table V only applies to completed configurations ; and although the scheme for these may be suggestive in connection with upbuilding, it does not enable the appropriate j values to be assigned, or the constitution to be determined directly for atoms containing incomplete groups. Thus the scheme suggests that 6 electrons in the L group would be distributed in 3 sub-groups of 2 electrons; but it is not necessarily legitimate to suppose that the electrons in these groups may be characterized by kj values of (1, 1), (2, 1) and (2, 2) which would apply to the completed L group with 8 electrons. The appropriate quantum numbers can only be determined from a study of the multiplet structure and Zeeman effect of the spectra, and will be discussed more fully in that connection.

The modified scheme for electron distribution is equally in harmony with the essential features of the development process in the upbuilding of atoms pictured by Bohr as that put forward by him originally, and so it is equally in accord with chemical considerations. Analogous sequences of elements correspond exactly on both schemes to analogous developments of electron groups; but on the new scheme the development occurs in a much simpler manner. As an illustration, the filling up of the underlying M group beginning with Sc (21) may be considered. The number of electrons increases from 8 to 18. The change is indicated by the first arrow in Table IV. A complete *reorganization* of the group occurs. In the modified scheme, the 10 additional electrons simply fill up the vacant $n3$, $k3$ levels, precisely 10 electrons $(4 + 6)$ being required. The added electrons referred to are bracketed in Table V. A precisely similar development occurs in the N $(n = 4)$ and O $(n = 5)$ levels, beginning probably at Y (39) and Lu (71). The rare earth sequence corresponds to the addition of 14 electrons $(6 + 8)$ in the N VI and N VII levels ($n4$, $k4$). This is indicated by the dotted brackets in Table V, while the dotted arrow of Table IV shows the reorganization in the original scheme.

As a whole the modified scheme may be said to be in complete harmony with the general quantum view of the structure of atoms. The problem of the constitution of any particular atom may be approached from Bohr's standpoint, considering the upbuilding by the successive addition of electrons to a nucleus, each electron entering a vacant level in which it is most firmly bound. In so far as this condition is complied with, there is a tendency for the electrons to form completed symmetrical configurations. These are shown in their most fully developed form in the electronic structure of the atoms of the inert gases.

It may be noted that the total number of electrons required to complete a group of quantum number n is $2n^2$ (2, 8, 18, 32 . . . for $n = 1, 2, 3, 4$). Each such group may be subdivided into n sub-groups with $k = 1, 2 \ldots n$, the number of electrons in each of these being $2(2k - 1)$ (2, 6, 10, 14 . . . for $k = 1, 2, 3, 4$); while the j sub-groups of these, with $j = k, k - 1$ have $2j$ electrons. The number of electrons completing the group is equal to the number of possible states for an n quantum orbit in a simple doublet atom.

For a discussion of the experimental evidence for the modified scheme reference must be made to the original papers; but the conclusions may be summarized. The X-ray emission line intensities seem to provide conclusive evidence for the presence of 2 and 4 electrons in L_{II} and L_{III} as inner atomic sub-levels over a wide range of atomic numbers, a sub-division also indicated for M_{II} and M_{III}. The absorption measurements confirm this, and suggest a distribution of the 22446 type for the 5M and the first 5N sub-levels. Considering the valencies, the chemical evidence is strongly in support of the upbuilding of the I, II, III L, M . . . P sub-levels as suggested by the final 224 distribution, and this is confirmed by the development of spectral type in proceeding across the periodic table. The chemical properties as revealed by co-ordination compounds also indicate the number 6 as characterizing the M, N and O V sub-groups. Magnetic considerations, which suggest 10 as the number of electrons in the M IV and V sub-levels, will be discussed fully later. It will then be seen that the modified Bohr scheme for the distribution of electrons is of great value in connection with the correlation of the magnetic and magneto-spectral properties of atoms. Independently of its intrinsic coherence, the scheme as a whole receives strong experimental support, not only directly, but also from the fact that it enables experimental data to be simply and naturally co-ordinated.

3. The Magneton

The magnetic moment corresponding to an orbital electron is equal to $\frac{eS}{c\tau}$, S being the area of the orbit (IV, 6), so, from (21),

$$\mu = k\frac{eh}{4\pi mc} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

In so far, then, as orbital electrons may be characterized by integral azimuthal quantum numbers k, the corresponding magnetic moments should be integral multiples of the unit $\frac{eh}{4\pi mc}$. Substituting the numerical values, this gives for the Bohr unit magneton

$$\mu_1 = 9{\cdot}23 \times 10^{-21} \quad . \quad . \quad . \quad . \quad . \quad . \quad (23.1)$$

or for the unit moment per gram atom (taking Avogadro's number $6{\cdot}06 \times 10^{23}$)

$$M_1 = 5{,}593 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23.2)$$

In 1911, from the then available results for atomic moments, Weiss concluded that there was a fundamental unit magneton. He had found that the saturation moments of iron and nickel at low temperatures were very closely in the ratio 11 to 3, from which a value for the unit was deduced (1,123·5 per gram atom). From later results, particularly on solutions, he concludes (1924) that the most probable value is

$$M_W = 1{,}126 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (24)$$

The empirical unit magneton has a moment very approximately one-fifth of the Bohr theoretical unit

$$\frac{M_B}{M_W} = 4{\cdot}967 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (25)$$

The Weiss magneton forms a convenient unit in terms of which to express deduced atomic moments; but that it is a fundamental unit—as will be discussed in connection with the later results—is very doubtful. The Bohr magneton would seem to have an unpromisingly large moment; but on consideration of the results in the light of further developments of the quantum theory, it seems that the Bohr magneton possesses fundamental significance as a physical unit.

It is of interest to calculate the numerical magnitudes of the fields arising from electrons moving in quantized orbits. Considering the field along an axis through the focus of the orbit and perpendicular to its plane, provided r is large compared with the dimensions of the orbit,

$$\begin{aligned} H &= \frac{2\mu}{r^3} = \frac{2k\mu_1}{r^3} \\ &= k\frac{9{\cdot}23 \times 10^{-21}}{r^3} \text{ gauss } (r \text{ in cm.}) \quad . \quad . \qquad (26) \\ &= 9{,}230\frac{k}{r^3}\text{gauss } (r \text{ in A.U.}) \end{aligned}$$

Thus at a distance of 2 A.U. the field arising from a $k = 1$ orbit will be of the order of 1,000 gauss.

The mean field will be a maximum at the centre of force about which the electron moves. Considering an elliptical orbit, using (21.1)

$$\mathbf{H} = \frac{e}{cr^3}\mathbf{v} \times \mathbf{r} \quad \overline{\mathrm{H}} = \frac{e}{mc}\frac{kh}{2\pi}\overline{\left(\frac{1}{r^3}\right)}$$

Now the time mean value of $\frac{1}{r^3}$ may be shown to be equal to

$\frac{1}{b^3}$, where b is the minor axis of the ellipse.

Using the relations of (19)

$$\begin{aligned} H &= \frac{eh}{2\pi mc} k \left(\frac{N}{nka_H} \right)^3 \\ &= \frac{eh}{2\pi mca_H{}^3} \; \frac{N^3}{n^3k^2} \\ &= 1{\cdot}23 \times 10^5 \frac{N^3}{n^3k^2} \text{ gauss} \quad . \quad . \quad . \quad . \qquad (27) \end{aligned}$$

The field at the centre of the normal (1, 1) orbit in the hydrogen atom is thus of the order of 100,000 gauss; as (26) shows, the field falls off very rapidly with distance. The maximum field arising from such an orbit is considerably smaller than those required in Weiss's molecular field theory, as has already been mentioned. As k increases, the field at a distance increases also, but the maximum field decreases. The fields arising from electrons in an atom at distances of the order of those between atoms and molecules will be no greater than those which can be applied artificially; but the fields inside the atoms may assume enormous magnitudes. The fields arising from the K orbit ($n = 1$, $k = 1$) will be the greatest, assuming values of the order of 10^5 for H ($N = 1$), 10^8 for Ne ($N = 10$), and for U ($N = 92$) nearly 10^{11} gauss! Purely speculatively, it might be suggested that the radioactivity of atoms of high atomic number may be connected with the possibility of these enormous magnetic fields at the nucleus. Normally, however, the two K electrons presumably balance magnetically, so that spontaneous radioactivity cannot be attributed to their magnetic fields; but it is of interest to note that Gaschler recently claims to have detected a marked increase in the rate of production of uranium X from uranium under the influence of intense electric discharges. This effect, if real, can hardly be accounted for by a direct action of bombarding electrons on the nucleus, and the question arises as to whether it might be due to the intense magnetic field at the nucleus resulting from the removal of one of the K electrons.

4. Symmetrical and Unbalanced Electron Orbits

From a magnetic point of view the transition elements possess particular interest owing to their paramagnetic characteristics. Paramagnetism occurs for other than transition elements, but not in the simple (polar) compounds where the elements enter as ions. Paramagnetism of atoms or ions is an indication of a lack of symmetry (and so of magnetic balance) of the electron orbits. In the formation of a simple compound there is a gain and loss of electrons by the constituent atoms, the outer electrons of the ion tending to assume an inert gas configuration. In NaCl, to take a simple example, the Na loses an electron, the Cl gains one; the electronic constitution of the ions will be similar to those of the inert gases Ne and A, which possess "completed" configurations. These completed configurations correspond to symmetrical balanced orbital systems with no resultant magnetic moment. The ions of transition elements, on the other hand, will possess all the asymmetry of the incomplete underlying group of electrons which is being built up in them. In $FeCl_3$ the Fe ion contains 23 electrons; of these 18 will be distributed among the K(2), L(8), MI(2), MII(2) and MIII(4) levels, as in A; the remaining 5 cannot form a completed symmetrical group, and the lack of balance among the electronic orbits gives the ion a resultant magnetic moment, and ionic paramagnetism occurs. The idea of associating the peculiar properties of the transition elements with the development of an underlying group of electrons was put forward by Ladenburg; it appears in its full beauty in Bohr's theory of atomic structure.

The whole question of the relation of atomic and ionic moments with electronic structure will be developed in detail later, and here only a preliminary indication is given as to the lines along which the interpretation is attempted, and as to the suggestiveness of the Bohr theory. Essentially ions or atoms with completed configurations, as in the inert gas atoms, would be expected to be diamagnetic; while those with unbalanced electronic orbits, such as are characteristic of incomplete groups or sub-groups, would be expected to be paramagnetic. The correlation of the magnetic moments with the structure is of outstanding interest. In so far as a successful attack on the atomic and ionic problem may be made, the outlook is hopeful for extending the underlying ideas to molecules in general, and to crystals; in this way not only may the range of application of the quantum theory be widened, but magnetism may play an important part in shedding light on the still obscure problem of molecular structure and chemical combination.

5. Spatial Quantization

The fixation of the stationary states of electronic systems presents a very difficult and complicated problem, which lies beyond the range of this book, but which will be found treated in detail in the works referred to at the end of the chapter. In spite of the generality of some of the methods which have been developed, any procedure must be regarded as tentative, and, to a certain extent, as being justified in so far as it leads to results in accordance with experiment.

In contradistinction to the classical theory, the quantum theory assumes that the energy of the system can only assume certain discrete values, which are fixed by the quantum numbers characterizing the state. The number of these is equal to the degree of periodicity of the system, and, at least in the simpler cases, they are integral. Consider an orbit in a hydrogen atom. If this is simply periodic only one quantum number n is necessary to determine the energy (which is the same whether the orbit is elliptical or circular). If, however, there are central perturbations of any kind (such as arise from the relativity change in mass) a second periodicity enters (corresponding to the precession of the orbit in its plane) and two quantum numbers, n and k, become necessary to fix the energy. In the presence of a field a further periodicity may be involved, and a third quantum number will be required. There are then three quantum degrees of freedom, equal to the number of degrees of freedom which an electron would be supposed to possess on the classical theory. The system is no longer " degenerate " (that is, requiring fewer quantum numbers to fix its energy state than its natural number of degrees of freedom).

In general, for a series electron orbit in an atom a field may arise from the atom core, or it may be applied externally. For a magnetic field the periodicity introduced corresponds to the Larmor precession ; the frequency of the precessional motion about the axis of the field being

$$\nu' = \frac{eH}{4\pi mc} \quad \text{(cf. IV, 8).}$$

Bohr assumes that the change of energy resulting is given by

$$\frac{\triangle E}{h} = n'\nu' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (28)$$

where n' is a whole number. This forms the basis of his treatment of the simple Zeeman effect.

The effect of an external magnetic field on the quantum conditions for the stationary states will here be considered from a slightly different standpoint, which leads to the same conclusions, and although perhaps less general, has the advantage of bringing some of the physical consequences of the theory into more immediate prominence. The basic idea of spatial quantization was put forward independently by Debye and Sommerfeld (1916). In the absence of a field, the orientation of the plane of an (n, k) orbit is indeterminate; a field, however, provides a direction with reference to which the orientation may be measured. Now the energy corresponding to an orbit depends on its orientation in the field, and in harmony with quantum ideas it would be anticipated that only certain orientations, determined by whole-number rules, would be possible, and moreover, that these discrete orientations would occur even in vanishingly small fields. The introduction of a third quantum number is justified by the new periodicity called into play by the field, and as the magnetic field gives rise to a precessional motion about its axis, it is natural to introduce tentatively a quantum condition for the angular momentum of the electron in the direction of this axis, corresponding, that is, to the resolved motion of the electron in the equatorial plane at right angles to the field. The variables defining the motion are separable and the quantum conditions may be applied in the (10.1) form. Let ψ be the co-ordinate defining the azimuth of the electron in the equatorial plane, ϕ the azimuth in the plane of the orbit. Let p_ψ be the generalized momentum corresponding to ψ; then, applying (10.1),

$$\oint p_\phi d\phi = kh \qquad \oint p_\psi d\psi = mh \quad . \quad . \quad . \quad (29)$$

where m is a whole number, so that for the angular momentum

$$p_\phi = k\frac{h}{2\pi} \qquad p_\psi = m\frac{h}{2\pi} \quad . \quad . \quad . \quad . \quad (29.1)$$

This procedure is justified by more general discussion, as a result of which Born gives the following rule: "In any system whose potential energy is invariant with respect to rotation about an axis fixed in space, the action variable is 2π times the component of the angular momentum about the axis. If the energy depends on this, its magnitude is to be quantized."

It should be noted—the point derives its importance in connection with the Zeeman effect—that in (29) the quantization is carried out for the system in the absence of a field. To make this clear, consider an orbit, and let r be the radius vector, ω the angular velocity of the electron, r' and ω' the corresponding resolved values in the equatorial plane. (29) is then equivalent to

$$m_0 r'^2 \omega' = m\frac{h}{2\pi}$$

using m_0 for the electronic mass.

When a field is applied

$$\omega' = \omega_0' + o \text{ where } o = \frac{e\mathrm{H}}{2mc}$$

The quantum condition is not, however, to be applied to ω',

$$m_0 r'^2(\omega_0' + o) \neq m\frac{h}{2\pi} \quad . \quad . \quad . \quad . \quad . \quad (30)$$

but to ω_0'

$$m_0 r'^2 \omega_0' = m\frac{h}{2\pi} \quad . \quad . \quad . \quad . \quad . \quad . \quad (30.1)$$

Alternatively expressed, in the presence of a magnetic field the same quantum conditions apply, all measurements being made with reference to a system of axes rotating with an angular velocity o—this being a quantum application of the generalized Larmor Theorem. The fact that the condition must be applied to ω_0' is a direct consequence of the principle of adiabatic invariance—the quantum integrals, such as $\oint p_\psi d\psi$ in (29), must be such that they are invariant with respect to slow changes in an external field.

The consequences of the quantum conditions as regards orientation are apparent from (29). Let a be the angle between the plane of the orbit and the equatorial plane; then, since $p_\psi/p_\phi = \cos a$,

$$\cos a = \frac{m}{k} \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

The orientation corresponding to $m = 0$ (the plane of the orbit parallel to the field) is ruled out because an electron rotating in such an orbit, on the application of an external electric field, would eventually collide with the nucleus, as appears from the theory of the Stark effect. According to the simple theory, then, an orbit of azimuthal quantum number k can take up k different orientations in an external magnetic field such that

$$\cos a = \frac{1}{k}, \frac{2}{k}, \ldots 1 \quad . \quad . \quad . \quad . \quad . \quad (31.1)$$

It will be seen later, in dealing with the Zeeman effect, that this simple treatment is insufficient to cover the experimental facts, as would indeed be expected, for in an atomic system both the core and series electron have magnetic properties; their mutual interaction has to be taken into account as well as the effect of the external field on each.

If the magnetic moment of an atom is related to the angular momentum in the simple and unique manner which theory suggests, $\boldsymbol{\mu} = \frac{e}{2mc}\mathbf{j}$ (cf. II, 60), it would follow from (29) or (31) that the resolved magnetic moment corresponding to an electron orbit in the field direction would be an integral multiple of the Bohr unit. Here again complications arise for atomic systems. Anticipating the discussion on the Zeeman effect and the Gerlach and Stern investigations, it may, however, be said that the experimental results indicate very strongly that the general mode of attack on the problem is correct, and also that in simple cases it leads directly to conclusions in accordance with what is observed. The evidence for discrete orientations seems absolutely definite; for atomic systems, however, the component of the magnetic moment in the field direction is not in general an integral multiple of the Bohr unit, though the moment and the unit are in the ratio of whole numbers. They have a rational fractional relationship involving small whole numbers for the simpler systems, larger numbers for the more complex. (See Ch. X.)

Although the results of (29) and (31) only apply to simple electronic orbits, deductions based on them in statistical applications, for example, will be true qualitatively, and, in general, approximately true quantitatively. The appropriate modifications may readily be made in the formulæ when required.

It will be seen from (31) that the number of orientations possible is equal to k, and as the electron can rotate in opposite directions, there are $2k$ states corresponding to each k orbit. The number of equally probable states for a k orbit (giving its "statistical weight," or a priori probability), on the simple theory, is therefore equal to $2k$; and since k can assume the values $1, 2 \ldots n$, the statistical weight of an n quantum orbit would then be equal to $n(n+1)$. This will not, however, give generally the number of possible states of an atom corresponding to a given n quantum electron, as will be apparent from section 2. In the particular case there considered (complete configurations) the number of possible n quantum states was $2n^2$. A fuller discussion of this question must, however, be deferred.

6. Statistical Applications

In Langevin's theory of a paramagnetic gas it was virtually assumed that the elementary magnet was rigidly fixed to the molecule as carrier; and that the thermal rotational motion of the molecules was the determinative factor as to the extent to which orientation occurred. In the expressions for the magnetization (IV, 15), the parameter a is given by

$$a = \frac{\mu\mathrm{H}}{k\mathrm{T}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

This assumes that there are two rotational degrees of freedom each with associated energy $\frac{1}{2}k\mathrm{T}$, or, writing U for the rotational energy, that

$$\mathrm{U} = k\mathrm{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

As Langevin himself pointed out, if U varied as some other function of T, it would be necessary to modify (32) accordingly. The type of modification introduced by supposing that the rotational energy can only assume certain discrete stationary values, related by quantum conditions to the frequency, may be illustrated by the comparatively simple treatment of Oosterhuis (1913). For the mean rotational energy, in place of kT, he writes, following Planck,

$$\mathrm{U} = h\nu/(e^{\frac{h\nu}{k\mathrm{T}}} - 1) + \tfrac{1}{2}h\nu \quad . \quad . \quad . \quad . \quad . \quad (33.1)$$

In this it is assumed that there is zero-point energy, the molecule possessing rotational energy at absolute zero. This agrees with the continuous absorption form of Planck's theory, but it is hardly in harmony with more recent quantum ideas. In the specific heat of hydrogen the rotational energy term is inappreciable below about 80° absolute, but this does not rule out the possibility of rotational energy independent of the temperature. The expression (33.1) must, however, be regarded as formal. If ω is the angular velocity, J the moment of inertia of the molecule,

$$\mathrm{U} = \tfrac{1}{2}\mathrm{J}\omega^2 = 2\pi^2\mathrm{J}\nu^2 \quad . \quad . \quad . \quad . \quad . \quad (33.2)$$

Combining (33.1) and (33.2) and making some further assumptions as to the variation of ν with T, Oosterhuis deduces approximately

$$\mathrm{U} = k\mathrm{T} + \frac{1}{12}\frac{h^2}{2\pi^2\mathrm{J}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (33.3)$$

Substituting this expression for kT in (32), and remembering that when a is small $\bar{\mu}/\mu = a/3$ (cf. IV, 15.3 and 15.4), there results

$$\chi_m = \frac{n_m\mu^2}{3k}\frac{1}{\mathrm{T} + h^2/24\pi^2k\mathrm{J}} \quad . \quad . \quad . \quad . \quad . \quad (34)$$

or

$$\chi_m = \frac{n_m\mu^2}{3k(\mathrm{T} + \theta)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34.1)$$

where

$$\theta = h^2/24\pi^2k\mathrm{J} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34.2)$$

The Weiss generalization of Curie's law is obtained, with a positive value for θ. This is found experimentally for many substances, and by choosing suitable values of J (e.g. $8{\cdot}7 \times 10^{-41}$ for $MnSO_4$, $1{\cdot}1 \times 10^{-39}$ for $MnSO_4.7H_2O$), fairly close quantitative agreement is obtained.

The question has been approached in a somewhat similar manner by Reiche (1917), who gives an elaborate mathematical treatment based on rather more satisfactory assumptions as to quantization. Again the theoretical and experimental curves may be made to fit over wide ranges of temperature. It must be noticed that the theory derives its interest in its application to solids at temperatures approaching absolute zero, where the modifications become of most importance. Here, however, the basic hypothesis—of elementary magnets virtually fixed to molecules which are free to rotate—is highly improbable, if not definitely untenable, so that, in spite of any theoretical-experimental agreement, it does not seem profitable to enter into the consequences in more detail.

The quantum theory indication that only definite orientations of the elementary magnets occur, which may be regarded as an experimentally verified fact, introduces modifications into the Langevin formula of far-reaching significance. Consider the simplest possible case of an electronic orbit, of moment μ, which can only set itself with its plane at right angles to the field. Let $\bar{\mu}$ be the mean effective magnetic moment. The ratio of the number of orbits with axes in the same direction as the field to those with axes in the opposite direction will be given by

$$n_1 : n_2 = e^{\frac{\mu H}{kT}} : e^{-\frac{\mu H}{kT}}$$

(Compare the derivation of equations IV, 14, and V, 6.)

The integrations involved in deriving the Langevin formula (IV, 14 and 15) are replaced by summations

$$\bar{\mu} = (\mu n_1 - \mu n_2)/(n_1 + n_2)$$

$$\bar{\mu}/\mu = (e^{\frac{\mu H}{kT}} - e^{-\frac{\mu H}{kT}})/(e^{\frac{\mu H}{kT}} + e^{-\frac{\mu H}{kT}}) = \tanh a \quad . \quad . \quad (35)$$

When a is small this gives $\left(\frac{\bar{\mu}}{\mu a}\right)_0 = 1$

$$\bar{\mu} = \mu a = \mu^2 H/kT \quad . \quad . \quad . \quad . \quad . \quad (35{\cdot}1)$$

This should be compared with IV (15.3).

(35) gives a curve of the same general form as the Langevin curve (Fig. 17) but with an initial slope three times as great.

These expressions were deduced by Lenz, and the function tanh a will be denoted by Le(a).

Ehrenfest supposed that the elementary magnetic orbits in a crystal could only set themselves at right angles to a fixed direction in the crystal. For a crystal powder, with elementary crystals distributed at random, for each constituent crystal

$$\frac{\bar{\mu}}{\mu} = \cos\theta \frac{e^{a\cos\theta} - e^{-a\cos\theta}}{e^{a\cos\theta} + e^{-a\cos\theta}}$$

Integrating over all the possible crystal orientations this yields

$$\frac{\bar{\mu}}{\mu} = \mathrm{E}(a) = \int_0^1 u \tanh(au)du \quad . \quad . \quad . \quad (36)$$

which gives a curve with initial slope

$$\left(\frac{\bar{\mu}}{\mu a}\right)_0 = \frac{1}{3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36.1)$$

but a maximum

$$\left(\frac{\bar{\mu}}{\mu}\right)_{\max} = \frac{1}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36.2)$$

in distinction to the Langevin and Lenz functions.

If it is assumed, in accordance with the simple quantum theory, that the magnetic moment in the field direction is integral, then, considering an orbit of moment corresponding to n units, which can set itself in the field so that its resolved moment in the field direction is n, $(n - 1)$, $(n - 2)$ . . . $-(n - 1)$, $- n$

$$\mathrm{L}_n(a) = \frac{\bar{\mu}}{\mu} = \frac{\frac{n}{n}e^{\frac{n}{n}a} + \frac{n-1}{n}e^{\frac{n-1}{n}a} + \ldots - \frac{n}{n}e^{-\frac{n}{n}a}}{e^{\frac{n}{n}a} + e^{\frac{n-1}{n}a} + \ldots + e^{-\frac{n}{n}a}}$$

$$= \frac{2n+1}{2n}\coth\frac{2n+1}{2n}a - \frac{1}{2n}\coth\frac{a}{2n} \qquad (37)$$

which reduces to L(a)—the Langevin function $\left(\coth a - \frac{1}{a}\right)$ when n is large. (37) gives

$$\left(\frac{\bar{\mu}}{\mu a}\right)_0 = \frac{n+1}{3n} \qquad \left(\frac{\bar{\mu}}{\mu}\right)_{\max} = 1 \quad . \quad . \quad . \quad (37{\cdot}1)$$

Although (37) is deduced on the assumption that the zero setting (with the plane of the orbit in the field direction) is not excluded, it shows the general nature of the modification to the Langevin function which the quantum theory would predict.

The curves corresponding to (37) are similar to the Langevin curves, but with greater initial slope. Bearing this in mind, the essential characteristics of the various functions may be summarized in the following table, where the initial slope $\left\{\frac{f(a)}{a}\right\}_0$ and the maximum values are given, a being equal to $\frac{\mu H}{kT}$.

	$\left(\frac{\bar{\mu}}{\mu a}\right)_0$	$\left(\frac{\bar{\mu}}{\mu}\right)_{\max}$
$L(a)$	$\frac{1}{3}$	1
$Le\ (a)$	1	1
$E\ (a)$	$\frac{1}{3}$	$\frac{1}{2}$
$L_n\ (a)$	$\frac{n+1}{3n}$	1

TABLE VI.

The essential interest in these expressions arises in connection with the derivation of the elementary moments. If paramagnetics could be investigated with high fields at low temperatures (giving large values of a) it would be possible to deduce the moments from the saturation intensity as well as from the initial slope of the $\left(\frac{\bar{\mu}}{\mu}, a\right)$ curves. Unfortunately gadolinium sulphate $Gd_2(SO_4)_3.7H_2O$ is the only substance which has been investigated over a sufficient range of values of a to enable both methods to be used. From the results (which will be considered in the next chapter) it emerges that

$$\left(\frac{\bar{\mu}}{\mu}\right)_{\max} \nless 2{\cdot}12 \left(\frac{\bar{\mu}}{\mu a}\right)_0 \quad . \quad . \quad . \quad . \quad . \quad (38)$$

For this substance, therefore, all the functions considered above are excluded except the Langevin function $L(a)$, and $L_n(a)$ with $n > 2$. The observed points lie fairly closely on a Langevin curve—or an $L_n(a)$ curve with n not too small (say $n > 5$).

The susceptibility results of the next chapter will be considered in connection with the derivation of atomic moments, particularly from the values for *a* small, in Chapter VII, where some of the relevant conclusions from the discrete orientation hypothesis will be discussed more fully. Here the emphasis has been laid mainly on the general nature of the complete $\left(\frac{\bar{\mu}}{\mu}, a\right)$ curve. It must be noted that although some of the functions are definitely excluded for gadolinium sulphate, it does not necessarily follow that they are not applicable to other substances.

In the first part of this section orientation was considered as being brought about by a definite mechanism involving molecular rotations. The mechanism is highly improbable. In the second part, where changes in the relative numbers of electron orbits with definite orientations were assumed to occur, resulting in a final statistical equilibrium distribution, it must, however, again be emphasized that the mechanism of the process is left completely unspecified.

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CHAPTER VI

SURVEY OF LATER EXPERIMENTAL RESULTS PARA- AND FERRO-MAGNETICS

1. Introductory

THE amount of work which has been done on the determination of magnetic susceptibilities is so great that it is impossible to do more than to give some indication of typical methods of investigation employed, and to discuss the results in detail in a few representative cases. For convenience, diamagnetics will be considered separately in Chapter XII. Paramagnetics have been examined in the light of the Langevin-Weiss theories, and the results are frequently most conveniently and concisely expressed in significant form in terms of magnetic moments per gram molecule deduced. The Weiss magneton, moreover, provides a convenient unit in terms of which to express the values arrived at, without it being implied that it is of fundamental physical significance. The older value of the unit—1123·5 erg/gauss per gram molecule—will be used for this purpose, as results are generally given in terms of it. (See Ch. V, sec. 3.) For a paramagnetic gas, on the Langevin theory, writing σ_0 for the saturation gram-molecular moment, N for Avogadro's number (cf. IV, 15.4),

$$\frac{\sigma}{\sigma_0} = \frac{\mu H}{3kT} \qquad \sigma_0 = N\mu \qquad Nk = R$$

$$\frac{\sigma}{H} = \chi_M = \frac{\sigma_0^2}{3RT} = \frac{C_M}{T} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; (1)$$

In (1) C_M is the Curie constant per gram molecule.

From (1)

$$\sigma_0 = \sqrt{3RC_M} \quad . \; . \; . \; . \; . \; . \; . \; . \; (2)$$

If p is the number of Weiss magnetons, R the gas constant ($8{\cdot}315 \times 10^7$),

$$p = \frac{\sigma_0}{1{,}123{\cdot}5} = \frac{1}{1{,}123{\cdot}5}\sqrt{3RC_M} = 14{\cdot}07\sqrt{C_M} \quad . \quad (2.1)$$

The magnetic moment per molecule is equal to $\frac{\sigma_0}{N}$, while p still gives the number of Weiss units per molecule. (The unit is $\frac{1,123\cdot5}{N} = 1\cdot85 \times 10^{-21}$.)

It should be noted that $\frac{\sigma_0}{N}$ may only be supposed to give the elementary moment if each molecule acts as a carrier of a single electronic orbit magnet. If each molecule acts as a carrier of n independently orientating magnets of moments $\frac{\sigma_1}{N}, \frac{\sigma_2}{N} \ldots \frac{\sigma_n}{N}$, corresponding to $p_1, p_2 \ldots p_n$ Weiss magnetons, then from (1)

$$\sigma_0^2 = \sum_n \sigma_n^2 \text{ and } p^2 = \sum_n p_n^2 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The formulæ (1) are found to hold closely over wide ranges of temperature for paramagnetic ions in dilute solutions. For solids, including ferromagnetics above the Curie point, the generalized Weiss expression applies.

$$\frac{\sigma}{H} = \chi_M = \frac{\sigma_0^2}{3R(T-\theta)} = \frac{C_M}{T-\theta} \quad . \quad . \quad . \quad . \quad (4)$$

giving as before

$$\sigma_0 = \sqrt{3RC_M}.$$

In deducing paramagnetic moments corrections have to be made for diamagnetic effects. In solutions the susceptibility of the solvent has to be taken into account. For an aqueous solution, let c_s be the concentration of the dissolved substance, χ the measured mass susceptibility, χ_s that of the substance, χ_w that of water. Then

$$\chi = c_s\chi_s + (1 - c_s)\chi_w \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

For water, according to concordant measurements of Sève, Piccard, Piccard and Devaud $\chi_w = -\cdot72 \times 10^{-6}$ at 20°. (This is probably correct to within ½ per cent.) The mass susceptibility χ_s can therefore be found and the gram-molecular susceptibility χ_M of the solute can then be deduced. To obtain the value for a particular ion (e.g. for Ni^{++} in $NiSO_4$) it is necessary to correct for the diamagnetism of other ions. This can be done with sufficient accuracy from the measurements mainly of Pascal, from which the following typical values may be deduced (referring to the gram ion):

F	11·5	SO_4	37
Cl	20	NO_3	18
Br	31	NH_3	14
I	45	H_2O	13
CN	11	Na	3·8
		K	10·6

TABLE VII.—GRAM-MOLECULAR SUSCEPTIBILITIES $-\chi_M \times 10^6$.

(These corrections are comparatively small for most paramagnetics; the gram-molecular susceptibility of $NiCl_2$, for example, being of the order of $5{,}000 \times 10^{-6}$ at ordinary temperatures.) The correction for the underlying diamagnetism of the paramagnetic ion or atom itself is unknown; but a plausible estimate of its magnitude may be made. Except for the heavier elements, such as Pt, the effect is usually negligible. (For Ni the correction would be of the order of ·1 per cent.)

In studying paramagnetics, then, whether gases, solids, or solutions, the usual procedure is to measure the susceptibility over a range of temperatures, the appropriate corrections being applied. If a linear variation of $\frac{1}{\chi}$ with T is found, Curie's constant may be deduced (from 1) and the Weiss magneton value p calculated (from 2). If the Weiss law (4) is followed, the experimental determination of θ forms the basis from which conclusions as to the molecular field may be drawn.

The investigations on paramagnetic gases, solutions and solids (including crystals) at ordinary temperatures will be considered in turn, the low-temperature work of Onnes then being dealt with separately. Finally a brief survey will be given of some of the salient characteristics of ferromagnetics. Attention will be directed mainly to the actual experimental results, the discussion of their interpretation being given in the next chapter.

2. Gases

The paramagnetic gases oxygen and nitric oxide are of particular interest, for in them the conditions for Langevin's theory to be applicable would be expected to hold most closely. Oxygen has been investigated over a range of temperatures from 20° to 450° C. by Curie, and, under a pressure of 100 atmospheres, by Onnes and Oosterhuis, from $+ 17°$ to $- 113°$ C., the Curie law being verified. Assuming the law to hold, the Curie constant may then be determined from observations at a single temperature. This has been done by Soné (1920) by a Gouy method, by Wills and Hector (1924) using their "magnetic balance" (which will be described in Ch. XII), and by other observers. The most accurate determination of the susceptibility is probably that of Bauer and Piccard (1920).

In their first method Bauer and Piccard employed an elaborated Quincke apparatus, of which the main features are represented in Fig. 20.

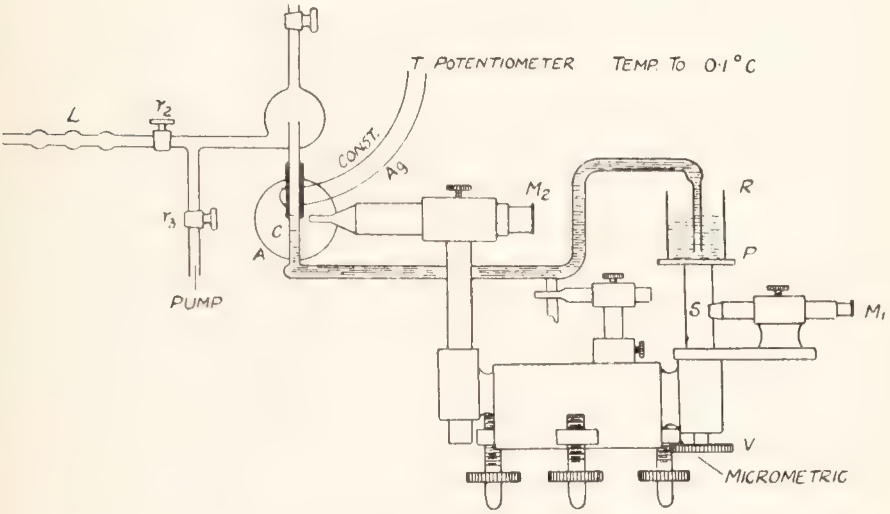

FIG. 20.—Bauer and Piccard's U-tube Apparatus (Method 1).

On the application of the field, the meniscus in the capillary C (3 mm. diam.) was brought back to its original level by raising the reservoir R (4 cm. diam.) by a micrometric device V; the meniscus was observed through M_2, the diffraction fringes due to a small straight filament lamp being utilized in making the settings. The temperature could be measured to ·1° C. by means of the constantan-silver couple T. The change in height of R was obtained from the reading of the glass scale S, marked in $\frac{1}{100}$ mm., observed through M_1.

Observations were made first for water in hydrogen (whose volume susceptibility is negligible, being about ·02 per cent. of that of water) and then in the gas being investigated. If h_0 is the change of level in the first case, h in the second, κ_0 the volume susceptibility of water, κ that of the gas,

$$\kappa = \kappa_0 \frac{h - h_0}{h_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

(The measurements were made relative to water, for which $\kappa_0 = \cdot 718 \times 10^{-6}$ at 20° was assumed.)

The greatest care was taken as to the purity of the water and the gases. The labyrinth L, consisting of small bulbs joined by narrow capillaries, was of such dimensions as practically to prevent any indiffusion of air, but in order to eliminate this possibility entirely, and also to avoid effects arising from variations in atmospheric pressure, a second apparatus was constructed on the **O**-tube principle. The reservoir R, in the form of a bulb, was joined by two tubes to C, one containing the gas, the other water. The long glass connecting tubes, of suitable dimensions, were bent in such a way that the reservoir side of the **O**-tube was mobile with respect to the capillary side. Otherwise, the general arrangement was the same as in Fig. 20. With such an enclosed system experiments extending over long periods were possible; this enabled a source of error to be discovered arising from the solution of the gas in the water. Without taking this into account, the calculated susceptibility might be as much as 3 per cent. too high. By making experiments under different conditions, however, it was possible to fix lower and upper limits, the latter by saturating the water first with the gas investigated. In this way, using fields from 12,700 to 27,000 gauss, the following values were found—

	$\chi_{20^\circ} \times 10^6$	
O_2	$< 107 \cdot 90$	$> 106 \cdot 95$
NO	$< 48 \cdot 6$	$> 48 \cdot 3$

The **U** and **O** tube methods are convenient in that the field need not be uniform, and its absolute value need not be known. Owing to the solution of the gas, however, only limits can be found, and although very accurate readings may be made, the results depend on differences $\left(\frac{h - h_0}{h_0}\right.$ is about $\frac{1}{5}$ for O_2, $\left.\frac{1}{14} \text{ for NO}\right)$.

A third method was therefore devised in which these undesirable features were eliminated. This was based on the measurement of the difference of pressure produced between two points of a gas, one of which is in a field H, and the other in a zero field, the difference being equal to $\kappa H^2/2$. (Cf. II, 37.)

The apparatus is shown in Fig. 21.

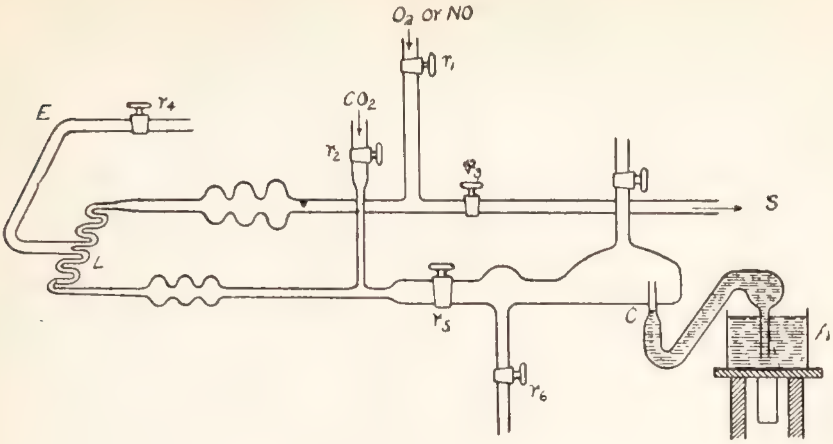

FIG. 21.—Bauer and Piccard's Gas Susceptibility Apparatus (Method 3).

LS, full of the gas under investigation, was open to the air. The pressure at L where the field was applied was transmitted to the water manometer A, by the very feebly diamagnetic CO_2 in the lower tube, the meniscus at C being read as before. The gases escaped via E. To prevent interdiffusion the labyrinth L has to be elaborately constructed. The appropriate dimensions may be approximately calculated. (Theoretical predictions were tested with air and NO, interdiffusion of which will be shown by the colouring due to the conversion of NO into NO_2.) Further, as the pressure gradient depends on the inhomogeneity of the field $\left(\frac{dp}{dl} = \kappa H \frac{dH}{dl}\right)$, the field must be uniform over the zone where the gases mix. The field was produced between truncated conical pole pieces (of angle 55°, to obtain strong fields) the faces being 45 mm. in diameter, and 6·4 mm. apart. The field was uniform to ·1 per cent. over a circular area 30 mm. in diameter. It was measured and explored by the inclined U-tube method (see Ch. III, sect. 2, eq. 10), so that the measurements were again made relative to water. This method has the advantage that no corrections have to be applied for solution of the gases, and that the results depend on the readings directly; the disadvantage that the field must be known, and uniform over a fairly large region.

Oxygen was very carefully investigated by the third method, and the ratio of the susceptibilities of O_2 and NO found, with the results—

	$\chi_{20^\circ} \times 10^6$	
O_2	$107{\cdot}8 \pm {\cdot}3$	$\frac{\chi_{20^\circ}\ O_2}{\chi_{20^\circ}\ NO} = 2{\cdot}212$
NO	$48{\cdot}7 \pm {\cdot}25$	

The various constants which may be deduced from these results may be collected. (It may be noted that $C_M = M\chi T$ where M is the molecular weight; $\sigma_0 = \sqrt{3RC_M}$.)

	Mass Susc. 20°. $\chi \times 10^6$.	Vol. Susc. 20° 760 mm. $\kappa \times 10^6$.	χT.	σ_0.	Weiss Magnetons p.
O_2 . . .	107·8	·1434	·03158	15,920	14·12
NO . .	48·7	·0609	·01427	10,330	9·20

TABLE VIII.—MAGNETIC CONSTANTS OF O_2 AND NO (BAUER AND PICCARD).

The degree of concordance between different observers is indicated by Table IX, which gives some of the results for oxygen.

	Temperature ° C.	$\chi \times 10^6$.	$\kappa \times 10^6$. (760 mm.).	χT.
Curie . . .	20– 450			·0307*
Onnes and Oosterhuis	– 113– + 17			·0303
Bauer and Piccard .	20	107·8	·1434	·0316
Soné . . .	20	104	·1386	
Wills and Hector . . .	20		·1447	

TABLE IX.—MAGNETIC CONSTANTS OF OXYGEN.

In the above table, Curie's original value for χT (·0337) has been recalculated (*) on the basis of ·72 instead of $·79 \times 10^{-6}$ for water. The measurements of Curie were carried out for oxygen at a pressure ranging from about 18 atm. (at 20°) to 45 atm. (at 450°), of Onnes at a pressure of 100 atm. The Langevin formula may no longer hold exactly at the higher pressures. If at the higher pressure $\chi_M = \frac{C_M}{T + \theta}$ the difference in the Bauer, Onnes χT values may be quite consistent with constancy of C_M. For a dilute solution of liquid oxygen in nitrogen Onnes finds $\chi T = ·0315$. The low-temperature work, however, will be considered further in section 5.

3. Solutions

Dilute paramagnetic solutions generally obey the Curie law, though there are exceptions. The solutions which have been most fully investigated are those of the simple compounds of elements of the first transition group (Ca–Cu). The paramagnetism may be attributed to the positive metallic ion, and it is usually found that the corresponding ionic susceptibility varies with the concentration of the solution. Some typical results will be considered here for a few solutions which have been examined over wide ranges of concentration. This will serve to indicate the nature and extent of the variations, and to give some idea as to how far the ionic values are significant, when deduced from the susceptibilities of solutions less completely examined.

Much of the work on solutions has been carried out under the inspiration of Weiss at Strasbourg, Zürich, Amsterdam and elsewhere, and by Cabrera and his collaborators at Madrid. The Quincke method, capable of great accuracy as developed in particular by Piccard, is usually employed, the apparatus being similar in type to that of Fig. 20. A modified Gouy method was adopted by Brant, in America, in her study of the cobalt salts.

In calculating the ionic moments it is assumed that the paramagnetic ions are all of one kind. In ions characterized by different Weiss magneton values $p_1, p_2 \ldots p_n$ are present, then from (3) the calculated p is given by

$$p^2 = \frac{1}{n}(n_1 p_1^2 + n_2 p_2^2 + \ldots)$$

where $n_1, n_2 \ldots$ give the relative numbers of ions, and $n = n_1 + n_2 + \ldots$ A variation of p with concentration might be expected; and the simple cases where there is only a single type of carrier will occur in general at limiting concentrations. The p values for the ions are calculated from the solution susceptibilities as already indicated, the appropriate corrections being applied. The elements from Cr to Cu will be considered, the atomic numbers, and the numbers of electrons in the ions being given; the charge on the ion being shown by an index figure (e.g. Fe^3 23 indicates the ferric ion Fe^{+++} containing 23 electrons).

Nickel (28).

$NiSO_4$, $NiNO_3$, $NiCl_2$ have all been examined over wide ranges of concentration; concordant values of p are found by different observers. Bruins has measured the susceptibility of

$NiCl_2$ over concentrations ranging from 0·6 to 22 per cent. and finds p constant to within ·4 per cent.

$$Ni^2\ 26 \qquad p = 16{\cdot}05 \pm {\cdot}03$$

Cobalt (27).

Partly depending on the thermal treatment they have received, though the exact cause is unknown, the salts of cobalt show different magnetic behaviour in solution; the ionic moment is in some cases practically constant, in others variable. With concentrations of the chloride ranging from ·5 to ·005 gm. mols. per litre, Trümpler obtained values for p in a series of experiments all lying between 24·53 and 24·59.

$$Co^2\ 25 \qquad p = 24{\cdot}56 \pm {\cdot}03$$

In other experiments both he and other investigators have found a moment varying between 24 and 25. Fig. 22 shows the results of Cabrera for the sulphate.

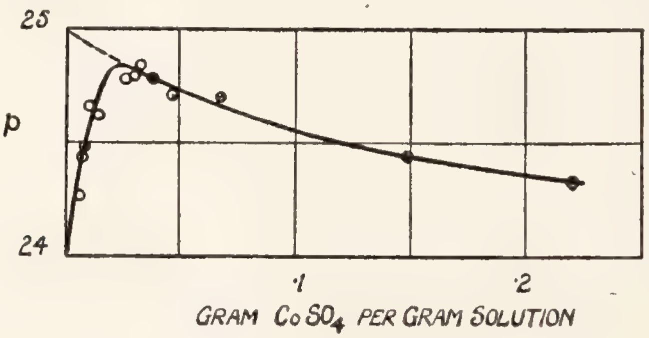

Fig. 22.

(It should be noticed that in this and the next graph the lines are drawn and extrapolated following Weiss.)

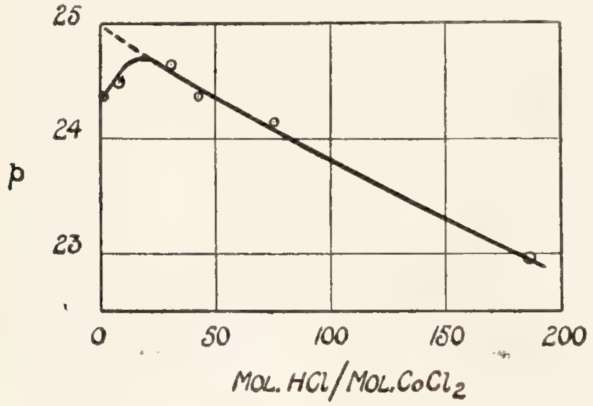

Fig. 23.

The sharp maximum in the curve is very striking. Starting with a ·7 per cent. solution of the chloride (·0531 gm. mol. per litre) and adding HCl, Cabrera found that the equilibrium between the different ionic carriers was displaced, as shown in Fig. 23.

At first the apparent moment is increased; but the linear form of the right-hand part of the curve suggests that there may also be a carrier of moment much less than 23 Weiss magnetons.

Iron (26).

Ferric Salts.—The solutions of these salts display properties corresponding to variability of the apparent ionic moment, analogous to those of cobalt, but somewhat simpler. Fig. 24 shows some results of Cabrera and Moles for $FeCl_3$.

The lower curve suggests the presence at low concentrations (when hydrolysis is complete) of a carrier with a moment of about 27; at higher concentrations 29 is approached. In curves 2 and 3 the effect of the addition of HCl to solutions of initial concentration ·052 and ·20 gm. mols. $FeCl_3$ per 1,000 gm. is shown. A carrier of moment about 29 is suggested.

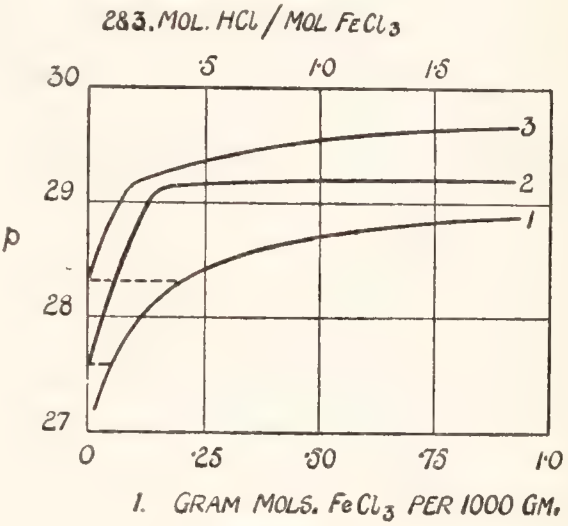

FIG. 24.

$Fe(NO_3)_3$ behaves very similarly; the ferripyrophosphate tends to 25 at low concentrations. $Fe_2(SO_4)_3$ gives a value slightly less than 26 at low concentrations, tending towards 27 at higher; addition of H_2SO_4 augments the apparent moment (cf. Fig. 24) to about 29. The extraordinary variability of the moments deduced from the ferric solutions makes it extremely hazardous to attempt to choose a value which might be supposed characteristic of the simple Fe^3 ion. Tentatively, however, the value of about 29 seems the most definitely indicated.

$$Fe^3 \; 23. \qquad p \doteqdot 29$$

Ferrous Salts.—These are like the salts of nickel in showing a remarkable constancy of apparent ionic moment. Weiss and Frankamp investigated solutions of $FeSO_4$ (0·37–20·7 per cent.) and $FeSO_4(NH_4)_2SO_4$ (0·25–17·5 per cent.) and deduce 26·54 magnetons, all the values being between 26·44 and 26·59. Other workers obtain the same result.

$$Fe^2 \; 24. \qquad p = 26{\cdot}5$$

Copper (29).

Five salts of copper, examined over a wide range of dilution by Mlle Jacobson, gave sensibly constant values between 9·5 and 9·6 ; at extremely low concentrations 9·75 has been attained, but the magnetic properties are still variable.

$$\mathrm{Cu}^2\ 27 \qquad p = 9{\cdot}6$$

Manganese (25).

Investigations have not been carried out at great dilutions, and Piccard has found that some of the salt solutions show a variation of magnetic properties with time. Over a fairly wide range, however (from ·6 per cent. upwards), for the chloride, sulphate and nitrate, Cabrera has found sensibly constant and equal values.

$$\mathrm{Mn}^2\ 23 \qquad p = 29{\cdot}4$$

Chromium (24).

Chromic Salts.—These occur in the green and violet varieties, and the constitution of the ions in solution is a somewhat involved chemical problem. Over a range from 1·3 to 19·8 per cent., $Cr(NO_3)_3$ (violet) gave p = 18·97 (18·86–19·07), and the sulphate from 1·2 to 10 per cent.

p = 18·96 (18·88–19·07), suggesting

$$\mathrm{Cr}^3\ 21 \qquad p \fallingdotseq 19$$

The complex green sulphate gave a considerably lower value 18·33 (irregular variations occur from 18·24–18·49 between 2 and 15 per cent.). The addition of H_2SO_4 to the solution at first decreases the apparent moment to a sharp minimum, after which it increases to an asymptotic value slightly greater than 19. The chlorides—$[CrCl_2(H_2O)_4]Cl$—green, and $[Cr(H_2O)_6]Cl_3$—violet, give 18·8. The apparent value tends to 19 on the addition of acid.

Chromous Salts.—Oxidation (which will tend to lower the apparent moment) is extremely difficult to avoid ; taking exceptional precautions, Cabrera examined the sulphate over concentrations ranging from ·16 to 1·16 per cent. and found a constant moment of 23·98 (23·89–24·04). The chloride, where oxidation is still more troublesome, gave 23·8.

$$\mathrm{Cr}^2\ 22 \qquad p \fallingdotseq 24$$

With very concentrated solutions Foëx has shown that the generalized expression $\chi_M = \frac{C_M}{T - \theta}$ must be used ; he then finds apparent values for the ionic moments in the neighbourhood of those deduced above—for $Co(NO_3)_2$ under different conditions, 25·03, 25·01 and 25·54; for $FeCl_2$, 27·04, 26·54, 27·02, 26·95.

Ferrous ammonium sulphate was investigated in some detail, but it was not found possible to deduce any relation between θ and the concentration, owing to the tendency of the solution to assume different magnetic states, the controlling factors being unknown. The Curie constant and θ seemed to be connected, and with a solution containing ·039 gm. Fe per gm. sol. θ varied linearly with p—from $+13°$ to $-52°$ as p varied from 26·0 to 28·5.

The variation of apparent moment with concentration and acidity does not seem to have been discussed with any degree of finality in relation to the nature of the ionic complexes present; the problem, which will only be touched on in the next chapter, is a difficult one chemically, and awaits further investigation. The magnetic moments of definite complex ions will be considered in Chapter XV.

Comparatively few solutions have been examined with the degree of completeness of those for which the results have been outlined; but the susceptibilities have been found for a large number, among them those of many rare earth salts, and ionic moments deduced. These will be given later, in connection with the general discussion on the subject.

Most of the salts in which the active element enters in the anion are diamagnetic; some are slightly paramagnetic, and in some others, when a correction is applied for diamagnetism of all the constituents, there seems to be a small residual paramagnetism. Potassium bichromate solution is remarkable in that it has been found by Weiss and Collet to have a susceptibility constant to within 2 per cent. between 14° and 50°; it gives for Cr (per gram atom) $\chi = 63{\cdot}3 \times 10^{-6}$, a value considerably smaller than most of those encountered above. For $p = 10$, for example, from (1) and (2.1), $\chi_{20°} = 1{,}740 \times 10^{-6}$.

It may be convenient to collect together probable ionic moments deduced from solutions. The table must, however, be used with caution in the light of the foregoing discussion of the results. The apparent moments are generally variable and it must be remembered that different magnetic carriers may be present in some cases, and that a particular ion (characterized by a given charge and given number of electrons) may have different possible magnetic states.

Ion.	Number of Electrons.	Weiss Magnetons.
Cr^3	21	19
Cr^2	22	24
Mn^2	23	29·4
Fe^3	23	29
Fe^2	24	26·5
Co^2	25	24·6
Ni^2	26	16·05
Cu^2	27	9·6

TABLE X.—Ionic Moments deduced from Solutions.

4. Solids

An enormous amount of work has been done on solid paramagnetics, whose susceptibilities have been measured over wide ranges of temperature. In considering the results there is a danger of becoming involved in such a mass of detail that essential features are obscured. If, however, too narrow a selection of typical results is made, there is a danger that these may be chosen because they happen to fit in with some theory. In this section an attempt will be made to strike a happy mean. The results will be given as they may be derived directly from experiment ; they will be ordered in the way suggested by theory as to convenient mode of expression, and as far as possible presented in a form suitable for later discussion.

Extended investigations have been carried out by Honda and Owen on the elements, and by Honda and Ishiwara on salts and oxides. Théodoridès has examined a number of salts, particularly, with greater precision, while Foëx has investigated a smaller number of substances with great care in attempting to elucidate special points. Jackson's work on the sulphates of nickel, cobalt and iron is more conveniently considered in the next section.

The usual method employed is to measure the force exerted in a non-homogeneous field. The apparatus used by Théodoridès and Foëx, represented in Fig. 25, may be briefly described. (For details, reference must be made to the valuable memoir by Foëx, which contains a very complete account of the procedure, and necessary precautions, in making precise susceptibility measurements.) A null method was used, the force being compensated by the attraction between current-bearing coils. The movable pendular system P, constructed of quartz, was suspended by silk threads *t*, from a frame F, whose height could be adjusted.

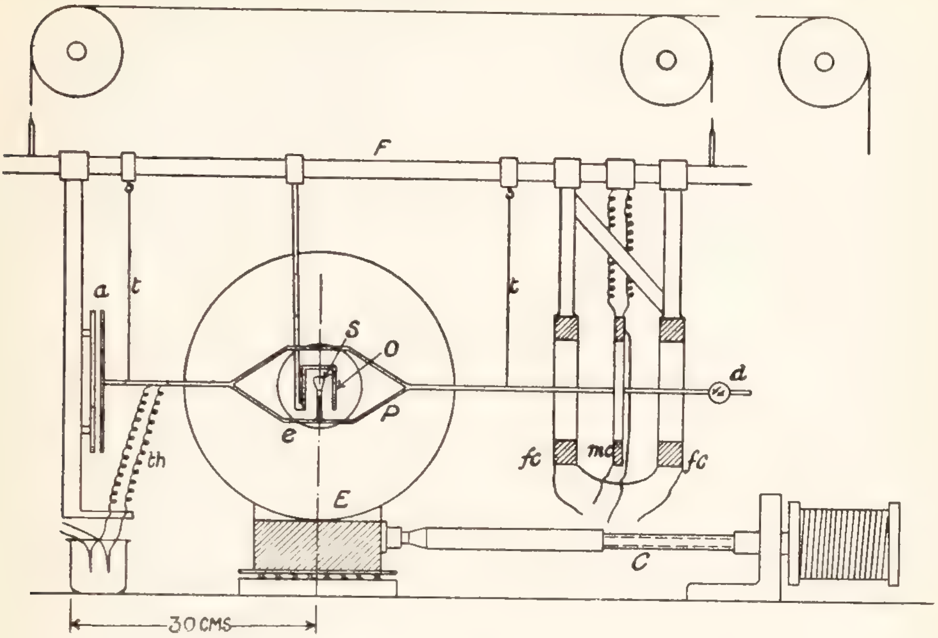

FIG. 25.

E*e*, Weiss electromagnet.
C, magnet control.
P, pendular system of quartz.
O, electric oven.
S, substance.
fc, *mc*, fixed and movable coils of electrodynamometer.
t, silk threads.
a, air damper.
th, thermocouple.

The substance S was supported on P between the poles of a Weiss electromagnet E*e*. P carried one of the plates of an air damping arrangement *a*, the thermocouple *th*, the movable coil *mc* of the electrodynamometer, and at *d* a mounted fibre or micrometer scale which was observed through a microscope so that the displacements of the system could be determined. P could move horizontally in a vertical plane perpendicular to the field and symmetrical with respect to the pole pieces. The magnet could be moved by the control C, so that the specimen could be brought to the region where the force was a maximum.

In Foëx's experiments the force on the substance investigated was compared with that on a standard of manganese pyrophosphate, by comparison of the currents through the fixed coils required to counterbalance the force, the current through the movable coil being kept constant.

The force depends on the field and its derivative $\left(f = \kappa \mathrm{H}_y \frac{\partial \mathrm{H}_y}{\partial x}\right)$. The accurate measurement of $\frac{\partial \mathrm{H}_y}{\partial x}$ presents great difficulties, and was evaded in the following way. The field was first measured with the utmost care both by the ballistic and electrodynamic methods. (Ch. III.) The susceptibility of a paramagnetic solution was then determined by the U-tube method. (A 33·75 per cent. solution of $MnCl_2$, giving $\chi_{17^\circ} = 39{\cdot}31 \times 10^{-6}$, was used.) This solution was then compared as above with the manganese pyrophosphate (which gave $\chi_{17^\circ} = 102{\cdot}2 \times 10^{-6}$), which was used as a standard in the subsequent experiments.

The sensitivity of the apparatus was such that a susceptibility of $\chi = 1 \times 10^{-6}$ could be measured readily with 2 gm. of the substance. The sensitivity of a torsional apparatus may be made 100 times greater, but for substances of moderate susceptibility the accuracy is usually much less.

" Ovens " and Dewar flasks of the usual type were employed, the former with openings at the lower end, as in the figure. With the Dewar flask the specimen was supported from the upper side of P.

Salts.—Over narrow ranges of temperature the susceptibility of salts generally follows the Weiss law $\chi_m = \frac{C_m}{T - \theta}$, and a graph of $\frac{1}{\chi}$ against T gives a straight line ; over wide ranges of temperature, however, there are often irregularities—the line may show a gradual curvature, or one or several more or less abrupt changes of slope ; in some cases, there is a jump from one line to another parallel one. C_m and hence p can, of course, only be deduced when there is a linear relation between $\frac{1}{\chi}$ and T. In Table XI are collected together some of the results of Théodoridès (T), Honda and Ishiwara (H), and of Foëx. Those of Honda and Ishiwara are given as interpreted by Weiss, who has, quite justifiably, utilized only linear portions of the graphs. In the first column are given, as before, the active ions with their resultant charge and number of electrons. It seems sufficient to give the Weiss magneton numbers p to 3 significant figures. In the table C_M is the Curie constant per gram molecule containing one gram atom of the active element. An example may be given. For $CoSO_4$, per gram, between 0° and 265° C.,

$$\chi_m = \frac{C_m}{T - \theta} = \frac{\cdot 02051}{T + 29{\cdot}92}$$

$$C_M = M \times C_m = (58{\cdot}97 + 32 + 4 \times 16) \times \cdot 02051 = 3{\cdot}179.$$

For ferric sulphate, the calculation is made for $\frac{1}{2}Fe_2(SO_4)_3$. The number of Weiss magnetons p is calculated as in (2.1).

Active Ion and Number of Electrons.	Observer.	Substance.	Temperature ° C.	Curie Constant per gm. mol. C_M.	θ.	p.
Cr^3 21	H	$CrCl_3$	− 167– 18			18·9
			250–550			18·9
Mn^2 23	H	$MnCl_2$	− 180–630			27·0
	T	$MnCl_2$	0–575	4·097	+ 3·1	28·5
	T	$MnSO_4$	0–270	4·267	− 19·03	29·0
			280–550	4·272	− 12·25	29·0
	F	$MnSO_4.4H_2O$ . . .	− 69–28			29·0
Fe^3 23	H	$Fe_2(SO_4)_3$	− 180–660			29·0
	T	$Fe_2(SO_4)_3$	0–250	4·245	− 79·5	29·0
			270–550	4·233	− 74·3	28·9
	H	$Fe_2(SO_4)_3(NH_4)_2SO_4$.	− 180–400			29·0
Fe^2 24	H	$FeCl_2$	− 182–200			25·9
		$FeCl_2.4H_2O$ . . .	− 180– 20			26·0
		$FeSO_4$	− 177–660			26·1
		$FeSO_4.7H_2O$ . . .	− 173– 23			26·0
	F	$FeSO_4.(NH_4)_2SO_4.6H_2O$	− 50– 16		+ 22	26·0
Co^2 25	H	$CoCl_2$	− 180– 0			25·1
			0–			24·2
	T	$CoCl_2$	0–325	3·151	+ 47·2	25·0
	H	$CoSO_4$	− 180– 0			24·2
	T	$CoSO_4$	0–265	3·179	− 29·92	25·1
			290–550	3·150	− 19·37	24·9
Ni^2 26	H	$NiCl_2$	− 120–360			16·1
	T	$NiCl_2$	0–130	1·301	+ 77·6	16·0
			150–500	1·448	+ 37·8	16·9
	H	$NiSO_4$	− 180–120			17·0
Cu^2 27	H	$CuCl_2$	− 140– 20			9·2
			20–500			10·0
		$CuSO_4$	− 120–700			10·0

TABLE XI.—MAGNETIC CONSTANTS OF PARAMAGNETIC SALTS.

The figures in the above table will be discussed later, but among points which may be immediately noted may be mentioned the striking agreement between the magneton values for the same ion deduced from different salts (though there are discrepancies); the tendency for p to be integral (in this connection, however, the results of Jackson in section 5 should be referred to) ; and the fact that the molecular field is positive for the simple chlorides, and negative for the sulphates (suggesting a marked dependence on the "anion").

While most paramagnetic salts follow the Weiss law over more or less extended ranges of temperature, there are some which behave anomalously, the paramagnetism being much smaller and independent of the temperature. An example is $KMnO_4$. From Ishiwara's measurements, correcting for diamagnetism, Weiss deduces for the atomic susceptibility of the Mn, $\chi_M = 64{\cdot}4 \times 10^{-6}$. $K_4Fe(CN)_6$ is diamagnetic, but correction for the diamagnetism of the K and CN indicates a residual paramagnetic atomic susceptibility of the Fe of $\chi_M = 29{\cdot}8 \times 10^{-6}$.

Oxides and Sulphides.—Results for the oxides are rather scanty and irregular, which is no doubt largely due to the difficulty of preventing chemical changes.

In general there are wide deviations from the Weiss law, and the *p* values given in Table XII (partly derived from Cabrera) have not the precision of those deduced from the salts. The following structures are assumed for the manganese oxides—

MnO $Mn = O$
Mn_2O_3 $O = Mn - O - Mn = O$
MnO_2 $O = Mn = O$

Probable Active Ion.	Observer.	Substance.	Temperature.	C_M.	θ.	p.
Mn^4 21 .	H	MnO_2	− 100–250			19·8
Cr^3 21 . .	H	$Cr_2O_3.7H_2O$	− 164– 19			19·1
Mn^3 22 .	H	Mn_2O_3	− 180–700			25·0
Mn^2 23 .	H	MnO	0–400			30·2
	T	MnO	0–316	3·808	−496	27·4
			316–550	3·534	−417	26·4

TABLE XII.—MAGNETIC CONSTANTS OF PARAMAGNETIC OXIDES.

The sulphides do not seem to have been examined over wide temperature ranges, so that no very definite conclusions can be drawn from the results. The need for further work is indicated by the following table giving the susceptibilities of the oxides and sulphides of vanadium at room temperature, in which χ_m gives the mass susceptibility, and χ_M the gram-molecular susceptibility, referred to a molecule containing 1 atom of vanadium.

	$\chi_m \times 10^6$.	$\chi_M \times 10^6$.		$\chi_m \times 10^6$.	$\chi_M \times 10^6$.
V_2O_5 . .	·86	77	V_2S_5 . .	12·56	1,645
VO_2 . .	3·73	310			
V_2O_3 . .	13·88	1,040	V_2S_3 . .	8·95	886
VO . .	50·06	3,350	VS . .	7·22	600

TABLE XIII.—SUSCEPTIBILITIES OF OXIDES AND SULPHIDES OF VANADIUM AT ROOM TEMPERATURE.

Elements.—In an investigation started by Honda and continued by Owen, the magnetic properties of nearly sixty elements were examined. The method did not differ essentially from that of Curie, so need not be described. Temperatures ranging from that of liquid air to about 1,200° C. were used. The elements were obtained in as pure a state as possible. One of the chief sources of uncertainty lies in the correction which must be applied for traces of iron. The total amount of iron present may be found by analysis, as was done. The iron, however, may not be "free," but partly or entirely combined in a non-magnetic form. The correction cannot therefore be calculated directly from the estimated iron content. The method adopted was as follows. With fields greater than that required to saturate the free iron (up to 25 kilogauss were used) curves were drawn showing the apparent susceptibility as a function of the field. These were found to be hyperbolic and could be represented by the equation

$$\chi = \chi_\infty + \frac{\sigma}{H} = f(H) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

σ being the constant saturation intensity of the "free" iron. (The "free" iron estimated in this way was usually found to be considerably less than the total iron content.) From the accuracy with which (7) represented the results, Honda and Owen concluded that the susceptibilities of the elements themselves which were investigated were probably all independent of the field. χ_∞ was taken as the susceptibility of the element itself. The procedure seems justifiable, but the actual magnitudes of the changes of susceptibility with temperature are of much more uncertain significance as characteristic of the elements, owing to the possibility of the iron changing its state of combination with temperature. The results for the paramagnetic elements are shown in Table XIV, χ and χ_{At} being the mass and gram atomic susceptibility at room temperature; C denotes constant, D and I decreasing and increasing suscepti-

	$\chi \times 10^6$.	$\chi_{At} \times 10^6$.	Variation with Temperature.
3 Li . . .	·5	3·5	C
11 Na. . .	·51	11·8	C − 170– 97
12 Mg. . .	·26	6·3	D*
13 Al . . .	·60	16·2	D − 170– 657 C 657–1,100
19 K . . .	·40	15·6	C* − 170– 150
20 Ca . . .	1·10	44·1	C − 170– 18
22 Ti . . .	1·24	59·5	D − 170– −40 I − 40–1,100
23 V . . .	1·5	76·5	C − 170– 500 I 500–1,200
24 Cr . . .	2·9	151	C − 170– 500 I 500–1,100
25 Mn . .	9	495	C − 170– 250 D 250–1,015
37 Rb . .	·07	5·97	C
41 Nb . .	1·3	131	D* − 170– 400
42 Mo . .	·04	3·84	I* − 170–1,200
44 Ru . .	·43	44	I* 550–1,200
45 Rh . .	1·1	113	I
46 Pd . . .	5·2	870	D
50 Sn . . .	·02	2·36	C 0–233
56 Ba . . .	·9	123	I − 170–18
57 La . . .	1·04	144	*d**
58 Ce . . .	15	2,100	D
59 Pr . . .	25	3,520	D
60 Nd. . .	36	5,200	D
68 Er . . .	22	3,700	D*
73 Ta . . .	·8	145	*d*
74 W . . .	·22	40·5	C*
76 Os . . .	·04	7·6	C
77 Ir . . .	·13	25	*i*
78 Pt . . .	·8	156	D*
90 Th. . .	·08	18·6	I − 170– 400
92 U . . .	2·6	620	*d*

TABLE XIV.—SUSCEPTIBILITIES OF PARAMAGNETIC ELEMENTS (HONDA AND OWEN).

bility with increase of temperature, small letters indicating that the change is slight. The table should be consulted in conjunction with that for diamagnetics, and the curve for the elements generally in Chapter XII. The temperatures are positive except where otherwise indicated. Where the temperatures are not stated, except for Li and Rb, where only a limited range was investigated, measurements were made (by Honda or Owen) at intervals over the whole range. The asterisks denote that the interpretation of the results is particularly doubtful owing to the presence of iron.

A few points connected with Table XIV may be briefly noticed. The tin there referred to as slightly paramagnetic is the ordinary white tetragonal variety. ("Grey" tin is diamagnetic with $\chi \times 10^6 = -\cdot35$.) The susceptibility remains practically constant up to the melting-point (233° C.), when there is an abrupt change, the liquid being diamagnetic, with $\chi \times 10^6 = -\cdot04$. Generally the paramagnetic elements showed no appreciable change in susceptibility at the melting-point.

Many of the elements are anomalous in that the susceptibility remains constant or even increases with increase of temperature. The "decreasing" elements do not follow Curie's law, but for some of them there are indications that, when appropriate corrections are made for underlying diamagnetism, a Weiss law would be obeyed within the (fairly wide) limits of experimental error over restricted temperature ranges. The rare earths Pt and Pd fall in this category, and Foëx has deduced from the results the following p values: Nd $p = 17$ (0°–470°); $p = 22$ (470° – 1,000°); Pd $p \doteqdot 9\cdot7$ (0°–1,200°); Pt $p \doteqdot 9$ (140°–1,200°). For Ce, Pr and Er p values of about 11, 14·5, and 14·5 are indicated.

Platinum and palladium have been investigated with great care by Foëx, using the apparatus already described (Fig. 25) for absolute measurements at ordinary temperatures, and the more sensitive torsional method for relative measurements at high temperatures. The $\left(\frac{1}{\chi}, T\right)$ curve is convex towards the temperature axis, which may be accounted for by a constant underlying diamagnetic susceptibility χ_D, so that

$$\chi = \frac{C}{T - \theta} - \chi_D \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Foëx's results for Pt and Pd (in close agreement with those of Kopp) are given in Table XV, together with those for Pt of

Onnes and Oosterhuis (O) at lower temperatures and of Honda (H) at higher.

	$\chi_{17^\circ} \times 10^6$.	Temp. ° C.	$C \times 10^3$.	θ.	$\chi_D \times 10^6$.	p.
Pd (F)	5·274	180– 460	3·044	−227	·545	8·03
Pt (O)	·973	−259– 17	3·32	−2,690	·141	11·45
(F)	1·035	16– 412	1·663	−1,124	·141	8·01
(H)		140–1,220	2·2		·141	9

TABLE XV.—Magnetic Constants of Palladium and Platinum.

It must be stressed that tables such as the above only give a general indication of the experimental results, which are frequently very complex and difficult to interpret; different observers working with great care often obtain different results with apparently similar material. Considering the $\left(\frac{1}{\chi}, T\right)$ curves for Pt, for example, Honda's results indicate a moment greater than 9 above 140°, and still higher values below—tending towards that deduced by Onnes. Kopp, on the other hand, using the same specimen as Foëx, finds 8 magnetons up to 500° C., and 9 above.

Crystals.—The first extensive study of single paramagnetic crystals—of great importance in connection with intrinsic field theories—seems also to have been made by Foëx. The translational apparatus was employed, the measurements giving the susceptibility along the axis which is parallel to the field; for details as to the setting and alignment of the crystals the memoir should be consulted. The most complete results were obtained with siderose—a rhombohedric ferrous carbonate with carbonates of the alkaline earths and manganese as impurities. The crystal was cut in the form of a cylinder with axis parallel to the ternary axis of the crystal. (The crystal weighed ·5773 gm., of which 75 per cent. consisted of paramagnetic carbonates.) The results of the measurements are shown in Fig. 26; the straight lines are represented by

$$\chi_{\perp} = \frac{\cdot 0332}{T + 103}$$

$$\chi_{\parallel} = \frac{\cdot 0332}{T - 60}$$

The interesting point emerges that while the magnetic moment is constant for different axes, θ—and hence the molecular field—may be quite different. Further results for crystals will be given in connection with the low-temperature work.

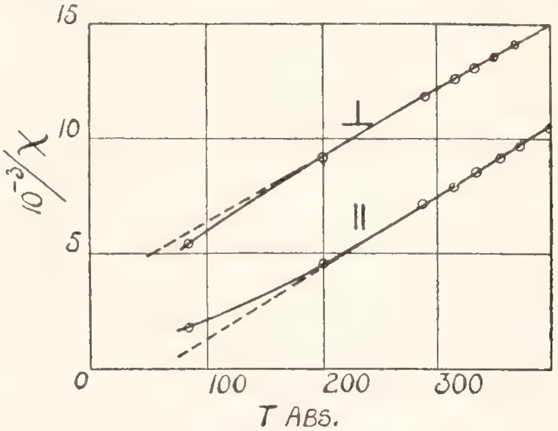

FIG. 26.—Susceptibility of Siderose ⊥ and ∥ to the Ternary Axis.

5. Low-temperature Investigations

It is possible to give only a very curtailed account of some of the more important results which have emerged from the remarkable series of experiments on paramagnetism at low temperatures which have been carried out by Onnes and his collaborators in the Cryogenic Laboratory at Leiden. Since the "effective field" depends on H/T, it will be much increased when T is small. At liquid hydrogen temperatures the phenomena may be intensified 15 to 20 times. Gases may be investigated without the necessity of using high pressures. Since $a \left(=\dfrac{\mu H}{kT}\right)$ may be large, there is a possibility of testing Langevin's theory as to an approach to saturation in paramagnetics, revealed by a deviation from the straight-line relation between the intensity of magnetization and a. Gadolinium sulphate has been examined from this point of view. Further, at low temperatures, where statistical classical mechanics breaks down, it becomes of outstanding interest to test how far the classical theories of paramagnetism are adequate, and what indication there may be of a need for the introduction of quantum ideas. Here the work on gadolinium sulphate and on oxygen will be considered, and then that on some substances showing anomalies of various types; finally the work of Jackson on a complete series of sulphates and double sulphates will be briefly outlined.

Gadolinium Sulphate.—$Gd_2(SO_4)_3.8H_2O$. This is one of the few substances which obey a Curie law down to the lowest temperatures—1·3° Abs. (The latest measurements indicate that there may be a very slight divergence corresponding to $\theta = 0{\cdot}26°$ in a Weiss equation.) It has been studied as a powder

—that is, a mass of very small crystals—by the cylinder method for low, and attraction in a non-homogeneous field for high susceptibilities. The susceptibility is given by $\chi = \cdot 0203/T$, which indicates a value for p of 39·2 magnetons. ($\mu = 7{\cdot}2 \times 10^{-20}$.)

Now

$$a = \frac{\mu H}{kT} = \frac{7{\cdot}2 \times 10^{-20}}{1{\cdot}37 \times 10^{-16}} \frac{H}{T} \text{ (see V, 17)}$$

$$= 5{\cdot}2 \times 10^{-4} \frac{H}{T}.$$

At 20·3° the magnetization was proportional to the field, but at 4·25° and 1·9° Abs., the proportionality broke down. At 1·31° C. with $H = 22{,}000$ gauss, values of a approaching 8 could be obtained. Plotting $\bar{\mu}/\mu$ against a, the points were found to lie very closely on a Langevin curve (Fig. 17), at the lowest temperatures an intensity corresponding to 84 per cent. saturation being reached.

Although a solid, therefore, the results for gadolinium sulphate, even at the lowest temperatures, are in complete accordance with those which would be expected if the carriers behaved like the magnetic molecules in Langevin's theory for a paramagnetic gas!

Ferric alum, $Fe_2(SO_4)_3.(NH_4)_2\ SO_4.7H_2O$, with $p = 29{\cdot}2$, and gadolinium ethyl sulphate, $Gd\ (C_2H_5.SO_4)_3.9H_2O$ with $p = 37{\cdot}3$, also obey Curie's law down to temperatures obtainable with liquid hydrogen (14·6° Abs.). The substances in this class, it may be noted, are all magnetically "dilute," the inert part of the molecules (the anion and the water of crystallization) being large compared with the active paramagnetic part (the Gd or Fe ions).

Oxygen.—The susceptibility of liquid and solid oxygen has been measured by Perrier and Onnes from the maximum couple exerted on an ellipsoid in a field, and by the cylinder attraction method; the Quincke method also being employed for the liquid. The general results for oxygen are exhibited in Fig. 27.

For the gas Curie's corrected results give $\chi = \frac{\cdot 0307}{T}$, while Onnes and Oosterhuis' measurements on the gas at 100 atm. between 170° and 290° Abs. fit the formula $\chi = \frac{\cdot 0306}{T + 2}$ or approximately a formula with $\theta = 0$. For the liquid, however, Curie's law is definitely no longer obeyed. The density of the pure liquid changes with temperature, and measurements were

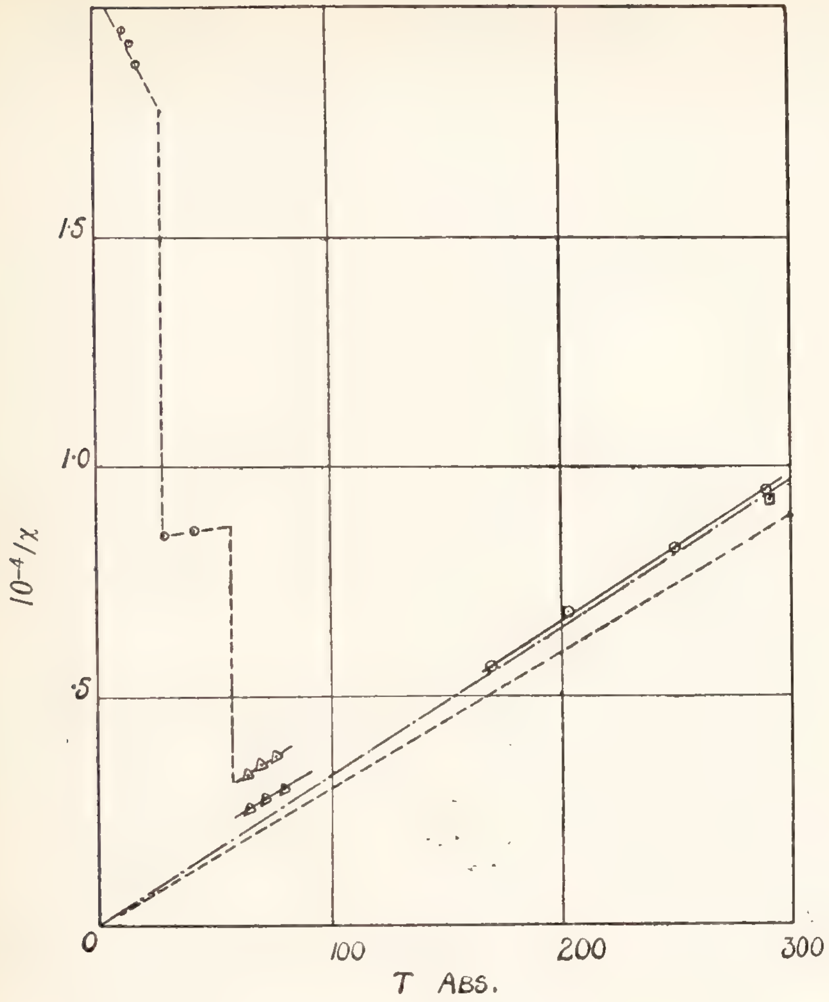

Fig. 27.—Susceptibility of Oxygen.

Gas ⊡ 1 atm. (Bauer and Piccard.)

----+ About 18 atm. Extrapolated (Curie).

—·—·— ,, ,, ,, and corrected (Curie).

—⊙— 100 atm. (Onnes and Oosterhuis.)

Liquid –△–––– ρ = 1·20–1·27. (Perrier and Onnes.)

Liquid diluted with liquid nitrogen.

–▲—— ρ = ·40. (Perrier and Onnes.)

Solid –⊙–––– (Perrier and Onnes.)

therefore made on mixtures of oxygen with the feebly diamagnetic liquid nitrogen, so that results could be deduced for the variation with temperature of the susceptibility of liquid oxygen of constant density. The measurements were carried out between 60° and 80° absolute. The observations agree with the formula

$$\chi = \frac{\cdot 0315}{T - \theta}$$

θ was found to be negative (negative molecular field) and to increase with the concentration of the oxygen.

ϱ.	θ.
·081	− 2·2
·138	− 4·5
·230	− 9·5
·401	− 16·3
·746	− 29·5

Approximately $\theta = - 40\varrho$, giving for the molecular field constant $N = - 1{,}270$, independent of the density. In all cases the relation between $\frac{1}{\chi}$ and T was linear. The Curie constant ·0315 leads to a p value for O_2 of 14·12.

Solidification (at about 57°) results in a sudden decrease in the susceptibility, and a large increase in θ is indicated; at 33°, however, a second magnetic allotropic modification is formed, whose susceptibility *increases* with decrease of temperature down to 13°.

Oxygen at low temperatures is certainly rich in phenomena of great significance for magnetic theory.

Cryomagnetic anomalies.—Although but few substances follow a Curie law, a great number—such as the salts discussed in section 4—follow the generalized expression $\chi = \frac{C}{T - \theta}$. Their behaviour can be accounted for by postulating a Weiss positive or negative molecular field proportional to the intensity of magnetization. As an example, dysprosium oxide, with $\theta = - 16°$, follows a Weiss law down to 14° Abs. At low temperatures, however, it is generally found that the relation between $\frac{1}{\chi}$ and T is no longer linear; anomalies indicated by a deviation from the linear relationship are referred to by Onnes as "cryomagnetic." A simple example is provided by $MnSO_4$, for which, down to about 70° Abs., $\chi = \frac{\cdot 0283}{T + 28\cdot 3}$. Below 70°, the increase in susceptibility is less than that indicated by the formula (the $\frac{1}{\chi}$, T curve being somewhat similar in form to the lower one of

Fig. 26), and the trend of the curve suggests a susceptibility almost independent of temperature near absolute zero. The anomaly with solid oxygen (χ decreasing with T) is still more striking. χ may increase more or less rapidly than a Weiss law would indicate, while in some cases the $\left(\frac{1}{\chi}, T\right)$ curves give indications of maxima and minima.

It may be noted here that although θ is positive for many substances (e.g. the chlorides—see section 4) at ordinary temperatures, a "real" Curie point has not been found for any of the substances investigated at low temperatures—none of them become ferromagnetic. Cryomagnetic anomalies always seem to supervene to prevent the $\left(\frac{1}{\chi}, T\right)$ curve cutting the T axis at a positive value of T.

Paramagnetic Sulphates.—Jackson has investigated the anhydrous and heptahydrated sulphates and the ammonium double sulphates of ferrous iron, nickel and cobalt over a range from room temperatures to those obtainable with liquid hydrogen (14° Abs.). The substances were chosen as forming three series of precisely similar constitution, so that the effect of a change in the active ion (Fe^2, Co^2, Ni^2) could be studied, and also the effect of different degrees of magnetic dilution.

The cylinder attraction method was used (Ch. III, eq. 3), the powdered substance being placed in the lower half of a cylindrical glass tube of uniform cross-section. The upper half of the tube was evacuated or filled with helium at low pressure. To the upper end was attached a glass rod fastened to a system floating in mercury. The cylinder was suspended so that the upper end of the "rod" of powder was on the axis of the poles of the magnet. Weights were then placed on a scale pan carried by the floating system, and the current through the magnet coils increased until the upward force due to the field restored the system to its zero position. The susceptibility could then be calculated from the equation

$$F = \tfrac{1}{2}\chi\frac{m}{l}(H_1^2 - H_2^2) \quad . \quad . \quad . \quad . \quad . \quad (9)$$

m and l being the mass and length of the "rod" of the powdered substance. The fields were measured in the usual way. H_2^2 was generally negligible compared to H_1^2.

The temperatures were obtained by means of baths of various liquefied gases boiling under known constant pressures, if necessary reduced, to enable lower temperatures to be reached.

Down to temperatures obtainable with liquid nitrogen (about 70° Abs.) all the substances followed a Weiss law, the molecular susceptibility, corrected for the diamagnetic part of the molecule, being given by $\chi_M = \frac{C_M}{T - \theta}$. The results are summarized in Table XVI, the Weiss magneton numbers (p) being calculated as in (2) and (2.1). The range of temperatures is 70–290 Abs.

	θ.	p.
$FeSO_4$	-31	25·53
$FeSO_4.7H_2O$	-1	25·84
$FeSO_4.(NH_4)_2 SO_4.6H_2O$	-3	27·5
$CoSO_4$	$-44·9$	25·2
$CoSO_4.7H_2O$	$-13·7$	25·04
$CoSO_4.(NH_4)_2 SO_4.6H_2O$	-22	24·75
$NiSO_4$	$-79·4$	16·9
$NiSO_4.7H_2O$	$+59$	14·62
$NiSO_4.(NH_4)_2 SO_4.6H_2O$	-4	15·9

TABLE XVI.—MAGNETIC CONSTANTS OF PARAMAGNETIC SULPHATES (JACKSON).

Below 70° Abs., except for the anydrous hydrated ferrous sulphates, deviations of various types from the Weiss law were found, as shown by the curves of Fig. 28 A, B, C.

Table XVI shows at once that there is no simple general relation between θ and the magnetic dilution. θ is negative for all the salts except the hydrated nickel sulphate, and this does not become ferromagnetic at low temperatures owing to the wide deviations from the Weiss law (Fig. 28, C, II). With the double sulphates (curves III) the susceptibility increases more rapidly with fall of temperature than the Weiss law would indicate (for the deviations Co > Ni > Fe); that of the hydrated nickel sulphate at first less and then more rapidly, the cobalt compound showing the same behaviour on a smaller scale, while the ferrous compound only shows a slight increase (curves II). The anhydrous sulphates give inflected curves, with a definite maxmium and minimum for Ni, which are also suggested for Fe (curves I).

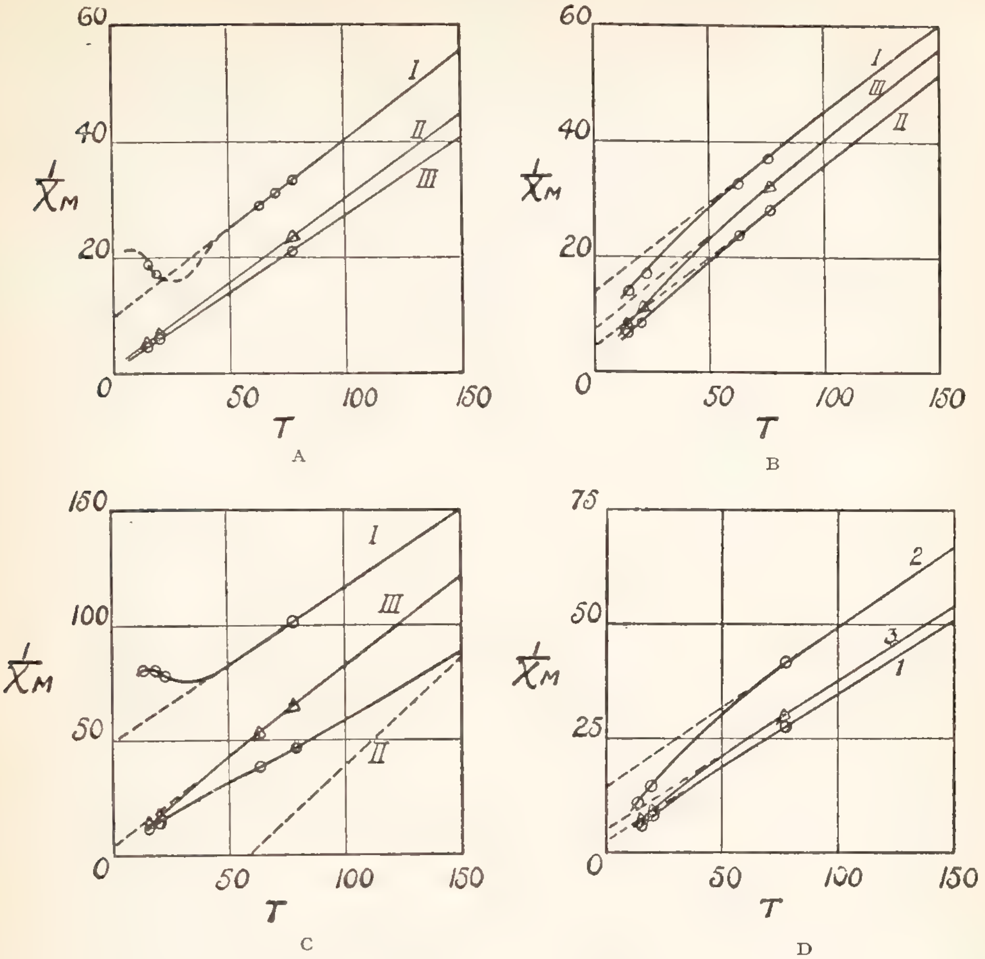

FIG. 28.—Susceptibilities of Paramagnetic Sulphates.

A

I. $FeSO_4$.
II. $FeSO_4.7H_2O$.
III. $FeSO_4.(NH_4)_2\ SO_4.6H\ O$.

B

I. $CoSO_4$.
II. $CoSO_4.7H_2O$.
III. $CoSO_4.(NH_4)_2\ SO_4.6H_2O$.

C

I. $NiSO_4$.
II. $NiSO_4.7H_2O$.
III. $NiSO_4.(NH_4)_2\ SO_4.6H_2O$.

D

$CoSO_4.(NH_4)_2\ SO_4.6H_2O$.
Crystal.

It becomes of great interest to see whether any light can be shed on the complicated behaviour observed with powders — crystals orientated at random — by measurements on the principal susceptibilities of single crystals. With this object in view Jackson investigated crystals of cobalt ammonium sulphate and nickel sulphate heptahydrate.

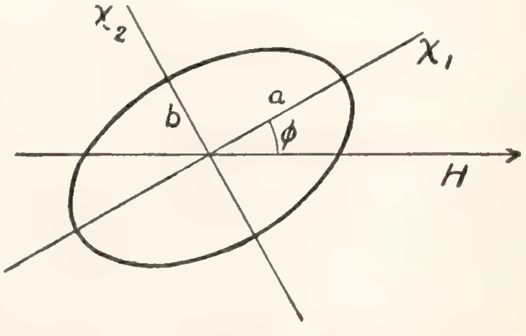

FIG. 28, E.

The non-homogeneous field method (used by Foëx) is unsuitable for low-temperature work, and the Weiss method was used in which the maximum couple exerted on a small disc-like cylinder of the crystal suspended in a homogeneous field is measured. The principle may be briefly indicated.

Let *a* and *b* (Fig. 28, E) be the directions of the magnetic axes (the corresponding susceptibilities being χ_1 and χ_2) of a disc suspended about a vertical axis, the field being in the horizontal plane of the disc. Let χ_r be the susceptibility in the field direction. Then the energy resulting from the introduction of the crystal in the field is given by

$$E = \tfrac{1}{2}\chi_r H^2 = \tfrac{1}{2}(\chi_1 \cos^2 \phi + \chi_2 \sin^2 \phi)H^2$$

$$\frac{\partial E}{\partial \phi} = \tfrac{1}{2}(\chi_2 - \chi_1)H^2 \sin 2\phi = C \quad . \quad . \quad . \quad . \quad . \quad (10)$$

C giving the couple exerted.

C is zero for $\phi = 0$ or 90°, and a maximum for $\phi = 45°$. By cutting discs in various directions with reference to the crystal planes, the directions of the magnetic axes may be found, and susceptibility differences; then from the mean absolute values (found for the powders) the absolute values of the principal susceptibilities may be determined. Details as to the rather elaborate torsional apparatus, the procedure, and calculations, are somewhat complicated, and reference must be made to Jackson's paper.

$NiSO_4.7H_2O$ crystallizes in the rhombic system, the crystals being elongated in the direction of the crystallographic C axis (χ_3). It was found that C_M was appreciably the same for the three principal magnetic axes, and the values found for θ were $\theta_1 = +59{\cdot}9$, $\theta_2 = +58{\cdot}0$, $\theta_3 = +59{\cdot}7$. The $\left(\frac{1}{\chi}, T\right)$ curves were all similar to the mean curve (Fig. 28, C, II).

The results for $CoSO_4.(NH_3)_2\ SO_4.6H_2O$ (monoclinic) are shown in Fig. 28, D (χ_3 corresponds to the symmetry axis); the straight-line regions give

$$\chi_1 = \frac{3{\cdot}138}{T + 9{\cdot}8} \qquad \chi_2 = \frac{3{\cdot}026}{T + 52{\cdot}4} \qquad \chi_3 = \frac{3{\cdot}126}{T + 14{\cdot}6}$$

Again the C_M values are approximately the same, as shown by the parallelism of the $\left(\frac{1}{\chi}, T\right)$ curves, and hence also the p values (24·9, 24·5, 24·8). At low temperatures the susceptibilities increase more rapidly than the Weiss law indicates (as in the mean curve), the deviations being greater the smaller the susceptibility (and the greater θ).

On the whole it may be said that the study of the crystals has not revealed phenomena hidden in the mean curves. It has, however, shown that while the Curie constant is approximately the same for different directions in the crystal, the molecular field may vary considerably.

6. Ferromagnetics

Above the Curie Point.—Above the Curie point the $\left(\frac{1}{\chi}, T\right)$ curves for iron, cobalt and nickel consist of a series of straight lines, characterized by different values of C and θ. The change of slope may be relatively abrupt, or there may be a gradual curvature, while in some cases there is a jump, indicating a discontinuous change in susceptibility. The values obtained for the Curie-point and transition-region temperatures differ considerably with different observers. The consideration of the results will be based on those of Weiss and Foëx (1911). These are summarized in Table XVII. The atomic number and atomic weight of the element are given; C and θ are the constants in $\chi = \frac{C}{T - \theta}$ referred to 1 gram, C_M refers to 1 gram atom, and p is calculated in the usual way.

	Temperature Range, ° C.	C.	θ.	C_M.	.
26 Fe β_1 .	774– 828	·0395	1,047	2·21	20·9
(55·84) β_2 .	828– 920	·0273	1,063	1·53	17·4
γ .	920–1,395	·072	−1,340	4·03	28·2
δ .	1,395–	·0045	1,543	·251	7·05
27 Co . .	1,170–1,241	·0217	1,404	1·28	15·9
(58·97)	1,241–1,303	·0182	1,422	1·07	14·55
28 Ni . . (58·63)	412– 900	·00555	645	·325	8·02

TABLE XVII.—MAGNETIC CONSTANTS OF IRON, COBALT AND NICKEL ABOVE THE CURIE POINT (WEISS AND FOËX).

There is no reason for supposing that α iron (below the Curie point) and β iron are constitutionally different, and indeed both have the same crystalline structure (body-centred cubic, with $d = 2{\cdot}88$ A.U.). At 920° there is a sudden decrease in susceptibility from $\chi = 210 \times 10^{-6}$ to $\chi = 28 \times 10^{-6}$. A transformation of the usual type seems to occur, which requires some hours for completion. γ iron is face-centred, with $d = 3{\cdot}60$ A.U. (Westgren and Lindh). It is noteworthy that θ is negative. At 1,395° there is again a sudden change in χ from $24{\cdot}1 \times 10^{-6}$ to $35{\cdot}1 \times 10^{-6}$. For δ iron, which is body-centred, the magnetic constants are not determined with precision. The p values given in the above table differ from those of Weiss for iron; he supposes the magnetic molecule to be Fe_3 and hence obtains values $\sqrt{3}$ times as large (36·0 for Fe β_1, and 30·0 for Fe β_2 for the triatomic molecule). Measurements of different observers agree well for β_1 and β_2, though there is considerable divergence as to the temperature at which the magnetic change of state occurs.

For nickel, between the Curie point (357°) and 412°, Weiss considers that there is a transition region, $\frac{1}{\chi}$ not being linear with T. Kopp (1919) has tested the linear law with great care between about 480° and 880°; and the results of eight independent investigators give values of p not differing by more than 6 in 800. Honda, however, finds $p \doteq 9{\cdot}1$ between 500° and 1,000°. His measurements were not of great precision, but the result agrees with those of Bloch and Renker above 880°, where they find 8·95 for p, and suppose that there is a second magnetic state of nickel—Ni β_2. It seems not impossible that the transition temperatures between different magnetic states may be considerably displaced by the presence of small quantities of impurities.

As has already been discussed, the Curie point is not well defined. For nickel, Weiss gives 357°, based on observations on the magneto-caloric effect, there being a discontinuity in the specific heat. The Curie temperature is usually deduced, however, by extrapolation from the susceptibility measurements at higher temperatures, and there are differences of the order of 20° between the values given by different observers. This should be borne in mind in connection with the following table, based on observations of Hegg, Bloch, Weiss, Hilpert and Dieckmann.

It will be clear from a consideration of the special case of γ iron (Table XVII), that, owing to the possible changes in magnetic state, the Weiss θ may be quite misleading in its indications as to the existence of a real Curie point; on the other hand it cannot be assumed that ferromagnetism would

Substance.	Temperature.	
	° C.	° Abs.
Fe (H)	758	1,031
Co (B)	1,137	1,410
Ni (H)	374	647
FeNi (H) . . .	365	638
Magnetite (W) . .	585	858
Pyrrhotite (W) . .	348	621
MnP (H and D) .	26	299
MnAs (H and D) .	45	318

TABLE XVIII.—CURIE TEMPERATURES.

occur even if θ is positive ; direct experiments must always be made.

Saturation at Low Temperatures.—According to Weiss's theory for ferromagnetics, discussed in Chapter IV, section 3, the atomic moments may be deduced directly from the value for the saturation intensity at absolute zero, when all the elementary magnets will be aligned. In collaboration with Onnes (1910) Weiss investigated the saturation intensity of Fe, Ni, Co and magnetite down to 20° Abs., the method being based on the measurement of the maximum couple exerted on an ellipsoid of the material, supposed isotropic. The magnetic "hardness" of cobalt, probably due to magnetocrystalline properties, prevented the attainment of saturation even in intense fields, and the measurements on magnetite were also invalidated, to a lesser degree, by some anisotropy. For Fe and Ni, however, it is possible to extrapolate to absolute zero without great uncertainty, particularly using a "corresponding state" curve (Fig. 18, Ch. IV). In Fig. 18 it will be noticed that the observed values all lie above the theoretical curve, giving σ_m/σ_{m_0} as a function of (T/θ). In calculating $f(T/\theta)$ the Langevin expression, $\sigma_m/\sigma_{m_0} = \coth a - \frac{1}{a}$, was used (cf. IV, 24), and it may be noted that if it is replaced by the quantum statistical function $L_n(a)$ (see Ch. V, section 6, equations 36 and 37), curves lying above that of Fig. 18 are obtained, which agree more closely with the observations, particularly when n is small. In all cases, however, there are systematic deviations.

Applying a rather uncertain correction for the change in density near absolute zero, Weiss deduced for the saturation moments per gram atom of Fe and Ni 12,360 and 3,370 respectively, numbers in the ratio of 11 to 3, which suggested the unit Weiss magneton of 1,123·5 per gram atom. The moment for cobalt corresponds approximately to 8 magnetons, but owing to the difficulties encountered with the metal itself, the value is more satisfactorily deduced by extrapolation from the results for alloys.

Of the ferromagnetic alloys various series have been investigated down to the temperature of liquid air: Fe-Ni (Hegg, 1910, and Peschard, 1925); Ni-Co (Bloch, 1912); Fe-Co (Preuss, 1912). For determining atomic moments, the method has the beauty of directness; the uncertainties involved in the extrapolations to absolute zero, however, make it very doubtful whether the Weiss magneton numbers deduced have the precision which is sometimes attributed to them. The results are shown in Fig. 29.

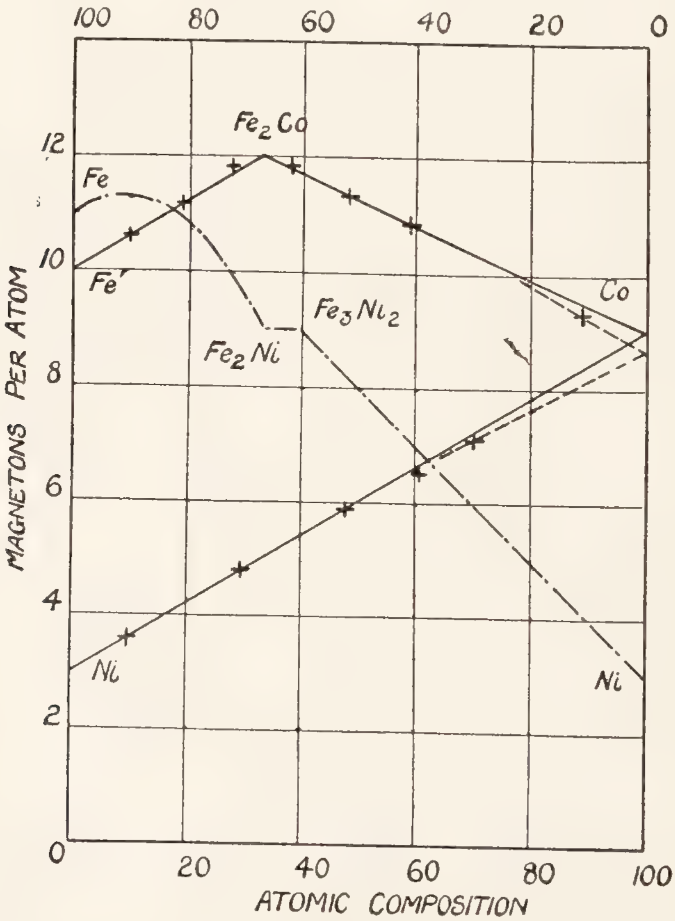

FIG. 29.—Magnetic Moments per Atom in Ferromagnetic Alloys.

———— Fe Co and Ni-Co.
—·—·— Fe-Ni.

The magnetic hardness of cobalt prevents accurate determinations on the Ni-Co alloys with more than 70 per cent. Co; extrapolation of the linear portion of the graph, however, leads to $p = 9$ for Co, which is also suggested by the Fe-Co alloys. Ferrocobalt, Fe_2Co, with a higher saturation intensity than Fe or Co (hence its use for electromagnets—see Ch. III) is strikingly indicated. The extrapolated p value for Fe (10) from the Fe-Co alloys is different from that for pure iron.

The Fe-Ni alloys show a more complicated behaviour, and two definite compounds Fe_2Ni and Fe_3Ni_2 seem to be indicated, both with 9 magnetons per atom. The usual p values for Fe and Ni (11 and 3) are suggested. A small percentage of Ni increases the mean atomic moment, though there is no indication of a definite compound.

The low-temperature investigations on which the curves of Fig. 29 are based involve great experimental difficulties. In addition to those already mentioned, errors may arise owing to the occlusion of gases in the metals. The directness of the theoretical interpretation of the results, however, makes it desirable that researches of this nature should be pushed to the fullest extent; in particular that measurements should be made at the lowest possible temperatures.

Properties of Thin Films.—The work of Maurain has already been referred to (Ch. IV, section 4). He found that when iron was electrolytically deposited in a field of 10 or 12 gauss, it was saturated. The hysteresis curves were practically rectangular, the coercive field H_e being about 20 gauss; the saturation intensity was somewhat low ($I_m = 840$). Kaufmann and Meyer obtained higher values ($I_m = 1{,}100$), using stronger fields (120 gauss), but still considerably less than those for ordinary iron ($I_m = 1{,}700$); the presence of a hydride may be the cause of the peculiarities. Maurain found that the magnetic moment of the deposit only increased proportionally to the thickness when this became greater than 80 $\mu\mu$; if, then, the external field was reversed (with $H < H_e$) the moment continued at first to increase in the original direction. The "magnetic field of contact" exceeded the external field. With thin intermediate deposits of neutral metals—Au and Cu—and an opposing external field of 1·65 gauss, the contact field was predominant until the neutral layer was 38 $\mu\mu$ thick. At this distance the residual "contact field" just neutralized the external field. The bearing of these phenomena on Weiss's molecular field theory has already been discussed.

Sorensen has also studied thin films of Fe, Co and Ni (1924) deposited by evaporation on tin or aluminium foils. The foils were rolled on threads into cylinders some 7 cm. long, and the magnetic properties along the film examined. The thickness of the films employed varied from 14 to 150 $\mu\mu$. For the thicker films the following values for the maximum intensity (I_m), residual intensity (I_r) and coercive field (H_c) were found.

	I_m.	I_r/I_m.	H_c.
Fe	1,700	·90	43
Ni	234	·56	62
Co	1,300	·62	34

(The approximate values for I_m for the metals in bulk are Fe 1,700, Co 1,300, Ni 400.) The coercive force was greater for thinner films, the increase being fairly abrupt at a definite film thickness.

	t.	H_c.
Fe	55 $\mu\mu$	$45 \longrightarrow 100$
Co	70 $\mu\mu$	$34 \longrightarrow 80$
Ni	200 $\mu\mu$	$56 \longrightarrow 75$

It has been shown that H_c increases with the number of crystals per unit length (Thompson—see Ch. XV, section 5). Sorensen concludes that H_c depends both on the crystal size and the film thickness, that I_m is independent of both of these, and that I_r depends on crystal size but not on film thickness.

Ingersoll and Vinney have recently prepared thin nickel films, by sputtering, which are devoid of ferromagnetic properties. Ferromagnetism, however, appears after suitable heat treatment, which has the effect of converting the films from an amorphous to a microcrystalline state.

Experiments of this kind, carried out with care, will undoubtedly throw light on coercive field phenomena; theoretical problems raised by the study of single crystals are attacked from a different direction.

Crystals.—Although there are comparatively few ferromagnetic crystals, the phenomena displayed by them are very various and complicated; it almost seems as though a small treatise might be written about the magnetic behaviour of each individual crystal which has been studied! The methods have been mainly developed by Weiss and his co-workers. A thin disc of known volume v, of definite orientation relative to the crystal faces, is cut and suspended by a torsion wire whose constants are determined. Mirror and scale arrangements of the usual kind are employed. In general the resultant intensity of magnetization is not parallel to the applied field, and the components parallel and perpendicular to the field are measured.

For $I_\perp$ the disc is suspended horizontally with the field in its plane. The couple is then given by

$$C = vI_\perp H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (11)$$

and $I_\perp$ corresponding to different directions in the disc may be found. For $I_{\parallel}$ the disc is suspended vertically ; the zero position is found for the field in the plane of the disc ; the field (i.e. the magnet) is then turned through a small angle ϕ, and the disc restored to its zero position

$$C \doteq vI_{\parallel}H \sin \phi \quad . \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

Corrections have to be applied for demagnetizing actions, and in (12) for the component perpendicular to the field. The corrections will be smaller the thinner the plates. When $I_\perp$ and $I_{\parallel}$ have been determined for various directions for differently cut discs, curves may be drawn giving the resultant intensity in magnitude and direction, for fields of different magnitudes, and different directions relative to the crystal as a whole.

Pyrrhotite (approximately Fe_7S_8) crystallizes in the hexagonal system ; it is much more easily magnetizable in its basal plane (the " magnetic " plane) than in a direction at right angles to this. In this plane the magnetic properties repeat themselves at intervals of 60°, but in various magnitudes, and Weiss concludes that the crystal is made up of elementary crystal components inclined to each other at this angle. The properties deduced for these elementary crystals will be considered.

In the magnetic plane saturation ($I_m \doteq 47$) occurs along one axis for about 15 gauss (OX, Fig. 30).

In the direction at right angles (OY) approximate saturation is only obtained with about 7,300 gauss. With small fields, as H rotates from OX to OY, the vector I traces out a path similar to that of the curve 1 (Fig. 30). I and H only coincide in direction along OX and OY. As H increases the curves ($1 \longrightarrow 2 \longrightarrow 3$) approach more nearly the " circle of magnetization " 4.

In a direction at right angles to the magnetic plane, Weiss concludes that fields of the order of 150,000 gauss would be required to produce approximate saturation. The phenomena shown by pyrrhotite—of which only the simplest, for " normal " crystals, have been outlined—are well accounted for by Weiss's intrinsic field theory, assuming molecular fields of the order of 100,000 gauss. Magnetite (Fe_3O_4, cubical) and hæmatite (Fe_2O_3, rhombohedric) have also been examined, and show similar properties, but directions of easy magnetization are not so marked, and the interpretation of the results is involved.

Iron crystals, which are difficult to obtain of reasonable

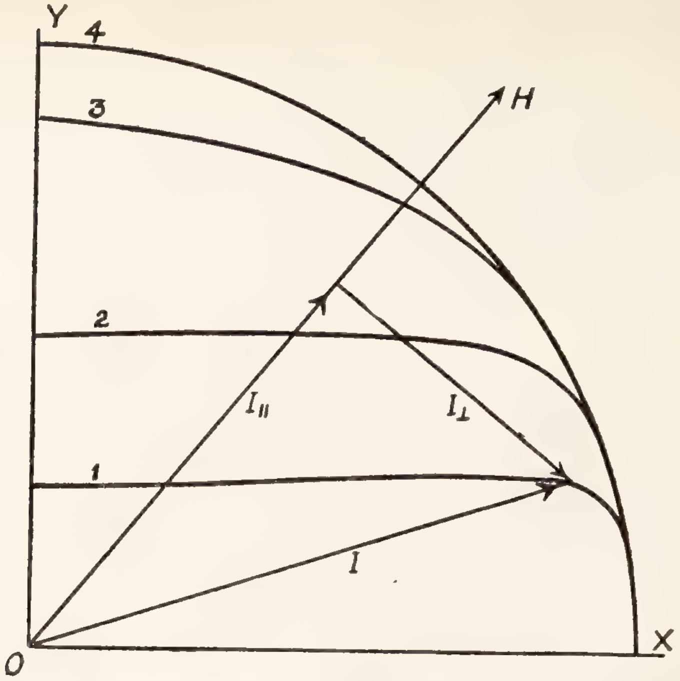

Fig. 30.—Intensity of Magnetization in the Magnetic Plane of Pyrrhotite.

1. H = 1,992. 2. H = 4,000. 3. H = 7,310. 4. H = 11,140.

dimensions, have been investigated by Beck, and recently by Webster. The results are in general agreement. Those of Webster may be briefly described. Iron has a cubical structure. Discs some 4·5 mm. in diameter, and ·35 mm. thick, cut parallel to (1, 0, 0) faces, were used.

The saturation intensity was 1,620, and this occurred for a field (corrected) of about 1,000 gauss. No variation in the intensity of magnetization I could be detected for different directions, except in the region just below saturation. Here the magnetization varied with a period of 90°, the maxima, along the quaternary axes, then exceeding the minima, along the diagonals, by about 15 per cent.

The $I_{\perp}$ and $I_{\parallel}$ curves enabled the resultant intensity I to be found; from this, and the known external field (corrected for demagnetization), the molecular field could be calculated. The molecular field depends on the intensity and a proportionality factor; since iron is cubical, it was assumed that the factor must be the same for the different axes, and this led to the conclusion that the component of the field along any axis was not simply proportional to the magnetization along that axis—otherwise I and H would coincide in direction, and no couple indicating an $I_{\perp}$ component would be produced. The results agreed with a molecular field proportional to $\cos^4 \psi$, ψ being the angle between I and the axis considered.

The molecular field was found to increase slightly with H, tending to a limiting value of 620 and 470 for discs from two different crystals. (The first had a larger amount of manganese, about ·4 per cent.; the second of phosphorus, about ·2 per cent., as impurity.) For the 470 disc the coercive field was about 4 gauss.

The dependence of the molecular field on the presence of impurities is noteworthy. Its low value compared with that for pyrrhotite is very striking, and indicates the need for fundamental revision of ferromagnetic theory. The importance of further experimental investigations, requiring the full collaboration of metallurgists and crystallographers, can hardly be over-emphasized.

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CHAPTER VII

DISCUSSION OF RESULTS
ELEMENTARY MOMENTS AND INTRINSIC FIELDS

1. Quantum and Weiss Magneton Numbers

IN the last chapter results of the measurements of the susceptibilities of a large number of substances have been considered. From many of them it is possible, on the basis of the Langevin-Weiss theories, to calculate the magnetic moment of the carriers concerned, and the question arises as to whether the values, deduced in this way, support the idea of the existence of a magneton, as a fundamental physical unit, some five times smaller than the theoretical magneton of Bohr. Undoubtedly, integral numbers of Weiss magnetons are often found (see, for example, Table XI). It must be remembered, however, in discussing the results, that with any predilection in favour of whole numbers—and the hypothesis *was* an attractive one—it is fatally easy, almost unconsciously, to obtain them, especially when the magneton numbers are large, and a certain amount of extrapolation or selection must necessarily be indulged in.

Since the value of the magneton was first arrived at from the low-temperature measurements on Fe and Ni, the whole numbers 11 and 3 obtained for them do not provide evidence for the unit. The numbers obtained for alloys (Fig. 29) all depend on considerable extrapolation (from liquid-air temperatures to absolute zero) of a rather uncertain character; and the value of 9 for Co depends on extrapolation which ignores some of the direct observations. Turning now to paramagnetic gases, which would be expected to obey the Langevin law most accurately, the numbers (14·16 for O_2, 9·20 for NO) definitely differ from integers by far more than can possibly be accounted for by experimental errors. Solutions in general do not give whole numbers, and even when extrapolations are made to limiting concentrations there are departures; and some of the most precise measurements (e.g., those of Trümpler on $CoCl_2$—24·53, not varying with concentration) yield values which cannot be reconciled with the Weiss unit. By postulating appropriate equilibria, the hypothesis might be upheld; but when there is no definite theoretical foundation for the unit, such postulates tend to assume a most unsatisfactory *ad hoc* character. The suggestion of a unit half as large need not be seriously considered.

Though many salts give whole numbers, even supporters of the magneton have found inexplicable divergences (e.g. Théodoridès, 28·45 for $MnCl_2$, 27·43 and 26·43 for MnO); while the very careful measurements of Jackson on the sulphates (Table XVI) yield values which lend no support at all for the unit.

Finally, the directly calculated values for ferromagnetics above the Curie point (Table XVII), except in the case of nickel, are non-integral; it is only by making somewhat arbitrary assumptions as to the magnetic molecule of iron (Fe_3) that integral magneton numbers are found.

It is only the more favourable evidence that has here been discussed; and it may be concluded that, invaluable as the Weiss magneton view has been in enabling results to be co-ordinated, there is no evidence for the existence of the unit as fundamental.

The quantum unit is five times as large; and it is at once striking that, with one exception, Weiss p values deduced are always greater than 5. The exception is nickel, for which the low-temperature saturation moment is 3. This might, at once, be an objection to the larger unit, if it had necessarily to be supposed that all the nickel atoms, in the solid at low temperatures, consisted of, or contained, carriers of the same moment. It is, however, by no means certain, or even probable, that all the ions in a metallic crystal are precisely similar; if in every five atoms, 2 had zero, and 3 the same moment, the elementary moment would be 5. While such a suggestion is purely tentative, it does indicate a possible explanation; and quantum possibilities may be explored without the feeling that there is a glaring initial anomaly.

In contradistinction to the Langevin theory, in which the elementary magnets may take up any orientation relative to the field, the quantum theory supposes that only certain discrete orientations are possible (Ch. V, sect. 5). For ease in comparison with experiment, the simplest procedure is to calculate, on the basis of the quantum theory, the p values which would be deduced corresponding to carriers possessing various moments measured in terms of the Bohr unit. The Weiss magneton number p is deduced from the Curie constant per gram molecule C_M from the expression (cf. V, 2)—

$$p = \frac{\sqrt{3RC_M}}{M_W} = \frac{\sqrt{3RC_M}}{1{,}123{\cdot}5} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Let b be the number of Bohr magnetons per carrier, and let M_B (= 5,593) be the Bohr unit moment per gram molecule. Since $\frac{\mu H}{kT}$ will be small in the cases considered, the formula appropriate to small values of a in deducing the Langevin expression may be used (IV, 16.3)—

$$\bar{\sigma}/\sigma_0 = a\,\overline{\cos^2\theta}$$

$\overline{\cos^2\theta}$ being the spatial mean value.

$$\bar{\sigma}/\sigma_0 = (\mu H/kT)\,\overline{\cos^2\theta} = (\sigma_0 H/RT)\,\overline{\cos^2\theta}$$

$$\bar{\sigma}/H = \chi_M = (\sigma_0^2/RT)\,\overline{\cos^2\theta} = C_M/T$$

$$C_M = \frac{\sigma_0^2}{R}\overline{\cos^2\theta} = \frac{(bM_B)^2}{R}\overline{\cos^2\theta} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Substituting in (1)

$$p = \frac{M_B}{M_W}\sqrt{3b^2\,\overline{\cos^2\theta}} = 4{\cdot}978\sqrt{3b^2\,\overline{\cos^2\theta}} \quad . \quad . \quad . \quad (3)$$

(A value for M_B/M_W slightly higher than in V, 25 is obtained as 1,123·5 is used for M_W instead of 1,126.)

If μ_H is the projected value of the magnetic moment in the field direction, expressed in terms of the Bohr unit, (3) may be written in the alternative form—

$$p = 4{\cdot}978\sqrt{3\overline{\mu_H^2}} \quad . \quad . \quad . \quad . \quad . \quad (3{\cdot}1)$$

If it is assumed that the carrier can set in any direction giving an integral moment in the field direction, including the value zero (following Debye, cf. V, 37 and 37·1)—

$$\sqrt{3b^2\,\overline{\cos^2\theta}} = \sqrt{3} \times \sqrt{\left\{\frac{0 + 2(1^2 + 2^2 + \ldots + b^2)}{2b + 1}\right\}}$$

$$= \sqrt{b(b+1)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4{\cdot}1)$$

For simple hydrogen-like electronic orbits the zero setting is excluded (cf. discussion of V, 31), and if the assumption is made, following Pauli's original treatment of the question, that this is general,

$$\sqrt{3b^2\,\overline{\cos^2\theta}} = \sqrt{(b+1)(b+\tfrac{1}{2})} \quad . \quad . \quad . \quad (4{\cdot}2)$$

Sommerfeld approaches the problem from a more experimental standpoint, considering the possible resolved magnetic moments in the field direction of atoms in an s state (that is, with the series electron moving in an orbit for which $k = 1$); these may be deduced directly from the behaviour of lines in the anomalous

Zeeman effect. For such atoms, the magnetic moment (given by the maximum resolved moment) is integral; for $b = 1$, $\mu_H = 1, -1$; for $b = 2$, $\mu_H = 2, 0, -2$; for $b = 3$, $\mu_H = 3, 1, -1, -3$, and so on, the number of possible settings being equal to $(b + 1)$, and the resolved moments ranging from b to $-b$ at intervals of 2. (A full discussion will be given in Ch. X.) Supposing that each setting is equally probable, it may be easily calculated that

$$\sqrt{3b^2\overline{\cos^2\theta}} = \sqrt{3\overline{\mu_H^2}} = \sqrt{b(b+2)} \quad . \quad . \quad (4.3)$$

The result of Debye (4.1) is what would be expected for isolated (and unrealizable) electronic orbits; that of Pauli (4.2) for hydrogen-like atoms with one electron moving in orbits with the azimuthal quantum number k equal to b. Sommerfeld's result (4.3) applies to atoms with a series electron in a $k = 1$ orbit; atoms with $b = 1, 2, 3$ . . . corresponding to those giving rise to series of doublets, triplets, quartets . . . respectively. Atoms in an *s* state are peculiar in that the total and resolved moments are integral, and have the same value in weak and strong fields, which may be taken to indicate that the systems are simple and definite, the relative orientation of the series electron orbit and the core remaining unchanged. For atoms with series electrons in $k = 2, 3$ . . . orbits, the Zeeman effect shows that the electron orbit and the core may take up different relative orientations, and that the resolved moments of the atom as a whole are not in general integral. The appropriate generalization of (4.3) is somewhat uncertain; adopting Sommerfeld's system of classification of spectral terms, however, it may be mentioned that the value of $\sqrt{3\overline{\cos^2\theta}}$ for an atom in a state characterized by an inner quantum number j is equal to $\sqrt{(j+1)/j}$ (see Ch. X).

The correct mode of application of the quantum theory to many of the systems constituting elementary magnets is as yet obscure, and almost every case requires special discussion. The general trend of p values which the theory would suggest is, however, undoubtedly to be found in the combination of (3) and (4); these are shown in the following table:

b Bohr magnetons	1	2	3	4	5	6	7
p' Pauli	8·6	13·6	18·6	23·6	28·5	33·6	38·5
p Sommerfeld .	8·6	14·1	19·3	24·4	29·5	34·5	39·5

TABLE XIX.—QUANTUM AND WEISS MAGNETON NUMBERS.

The calculations are all made on the assumption that the external applied field alone determines the orientation; this must be borne in mind. Further, following the usual procedure, it is supposed that the elementary magnets take up settings in accordance with a Boltzmann temperature equilibrium distribution, the details of the processes by which the necessary changes in orientation take place being left entirely undefined.

2. Elementary Magnetic Moments

Paramagnetic Salts.—The paramagnetic salts, in solution, or as solids, in some ways present the simplest problem, for the question as to the nature of the carrier can generally be definitely answered. It consists of the ion of the active element, and it will be clear from the results for Mn^2 and Fe^3 (Tables X and XI), and others to be given, that the magnetic moment of an ion is primarily a function of the number of electrons it contains. (This appears to have been pointed out first by Kossel.) This simply means that although the relative firmness of binding of electrons in different possible orbits may vary with nuclear charge, it frequently happens that the quantum numbers characterizing the electrons in ions in their most stable state, with the same number of electrons, but different nuclear charge, are the same, and hence the magnetic properties are the same also.

For many salts in solution (e.g. $NiCl_2$, $FeSO_4$) the apparent ionic moment (here for Ni^2 26, Fe^2 24) is independent of the concentration. It would, therefore, appear that the "magnetic freedom" of the ion, or its ability to acquire its different possible resolved moments in the field direction, is independent of the degree of ionization, that is, of the closeness of association of the positive and negative ions, into systems which, from the point of view of osmotic pressure and allied phenomena, behave as single molecules. In a simple molecule in solution, such as $NiCl_2$, the conclusion seems unavoidable that the active magnetic ion (or its effective magnetic part) is capable of independent change of orientation—a conclusion which does not seem intrinsically improbable. The same arguments, however, must also apply to the ions in the simpler typical paramagnetic solid salts. The ions with a fixed mean position on a crystal lattice must be capable of a change in orientation even at very low temperatures. This will be discussed more fully later.

In solution a change in the constitution of the ions may be brought about by suitable reagents. An example is provided by $CoCl_2$ (see Fig. 23). Addition of HCl will result in the formation of ions of the $(CoCl_3)^-$ and $(CoCl_4)^{--}$ type; and this is signalized magnetically by a change in the apparent moment of the Co. Mere change in concentration may be accompanied by quite complicated chemical change. For some solutions there is a marked tendency for hydrolysis to occur for high dilutions. Ferric chloride gives an example. Hydrolysis may be accompanied by the formation of complex ions, with corresponding variation in the apparent magnetic moment (Fig. 24). Increasing concentration, or the addition of HCl, will result in the formation of more $FeCl_3$ molecules. For each salt there is a separate chemical problem; and the chemical and magnetic changes must be studied together before the magnetic properties of solutions can be adequately treated. For the present purpose, the magnetic moments of the simple ions are required; and the numbers deduced by Weiss for limiting concentrations may be assumed to give for these an approximate—but only an approximate—value.

In solid salts the ions have a more definite character. From the variation of the results for the moment of the same ion in different salts, or even in the same one, it is evident that disturbing factors may enter. The variations may arise partly from the ions not all being the same, and also, in the light of the quantum discussion, from the existence of intrinsic fields of variable character. Again, the results can only be supposed to give an approximation to the true value for the simple ion primarily concerned.

With these preliminaries the probable values for the ionic moments of the first transition series of elements, based partly on the results of the last chapter, and partly on data collected by Dorfmann and Cabrera, may be considered. The Weiss magneton values are given to the nearest whole number. The measurements on individual substances, of course, yield values much more precise, but it is here being assumed that, although the ions themselves may have a precise and definite moment, values differing from this may be deduced from the measurements owing to the effect of various disturbing factors. N is the number of electrons in the ion.

The "observed" moments in general certainly do not agree closely with the quantum values of Table XIX, and when there is exact accordance for a particular substance, this can only be regarded as fortuitous, especially as the structure of the ionic carriers is in general considerably more complicated than that of the systems for which the quantum calculations have been made. Bearing this in mind, the agreement as to order of

N	18	19	20	21		
Ion	K^1 Ca^2 Sc^3 Ti^4	Ti^3		V^2	Cr^3	Mn^4
p	0	9		9	19	20

N	22	23	24	25	26	27	28
Ion	Cr^2 Mn^3	Mn^2 Fe^3	Fe^2	Co^2	Ni^2	Cu^2	Cu^1 Zn^2
p	24 25	29 29	26	25	16	9	0

TABLE XX.—Approximate Ionic Magnetic Moments of the first Transition Series of Elements.

magnitude is most striking, and can leave little doubt as to the essential truth of the basic ideas involved in the quantum treatment—that the Bohr magneton exists as a fundamental physical unit, and that systems possessing a magnetic moment tend to assume definite discrete orientations relative to an applied magnetic field.

As the number of electrons increases from 18 to 23, the magnetic moment increases from 1 to 5, as though each electron added to the inert gas type of configuration may increase its moment by one Bohr unit. In V^2 ($p = 9$, $b = 1$) it would appear that two of the three added electrons balance magnetically. For an ion with 28 electrons—again a " closed configuration "—the moment is zero, and the moment increases with *decrease* in the number of electrons. Pauli's " reciprocity law " (Ch. V, sect. 2) may be recalled. The p values, however, diverge widely from the quantum numbers corresponding to whole numbers of Bohr magnetons; for Cu^2 probably $b = 1$; nothing definite can be said about Ni^2; while Co^2 is quite anomalous in having a moment corresponding to $b = 4$, although it has only three electrons less than the completed configuration, and the spectroscopic evidence definitely points to an odd magnetic moment. The structure of the ions of the transition elements at the right of the periodic table is, however, very complicated, and divergences from any simple theory would be expected. Further discussion of the question may most usefully be postponed until the attempt is made to correlate the magnetochemical ionic moments with those deduced from spectra (Ch. X).

The susceptibilities of compounds of the rare-earth elements have been measured by Cabrera and St. Meyer, great care being taken as to purity of the materials, though in some cases this is difficult to ensure. Cabrera's measurements were made on the octa-hydrated sulphates; and in the calculation of the p values it was assumed that, owing to the great physical and chemical similarity of the elements, these sulphates would all obey the Curie law, as $Gd_2(SO_4)_3.8H_2O$ is known to do. The Weiss magneton number can then be calculated from the formula (see VI, 2.1) $p = 14{\cdot}07\sqrt{\chi_M T}$; for measurements at room temperatures (17°) $p = 7{\cdot}58\sqrt{\chi_M \times 10^3}$, χ_M being the susceptibility per gram molecule containing one gram atom of the active element. The difference in the values for θ for the sulphates of iron, cobalt and nickel (Table XVI) makes it doubtful whether the procedure is justifiable, and the p values deduced can only be regarded as approximate. St. Meyer's values were obtained in a similar manner, though some of the measurements were made on oxides. The results are given in the following table.

N	54		55		56	57	58	59	60
Ion	La^3	Ce^4	Ce^3	Pr^4	Pr^3	Na^3	—	Sm^3	Eu^3
Cabrera . .			11·4		17·8	18·0		8·0	17·9
St. Meyer . .	0	·8		13·8	17·3	17·5		7·0	18·0

N	61	62	63	64	65	66	67	68	
Ion	Ga^3	Tb^3	Dy^3	Ho^3	Er^3	Tu^3	Yb^3	Lu^3	Hf^4
Cabrera . .	40·0	47·1	52·2	52·0	47·0	35·6	21·8		
St. Meyer . .	40·2	44·8	53·0	51·9	46·7	37·5	22·5	0	0

TABLE XXI.—IONIC MOMENTS OF RARE-EARTH ELEMENTS.

The values for the moments are plotted in Fig. 31, the approximate number of Bohr magnetons (b) corresponding to the number of Weiss units being given on the scale.

The p values are not integral, nor do they agree, except very roughly, with the numbers of Table XIX. On the other hand, the orders of magnitude of the moments are what would be expected with the quantum theoretical unit. The moments are zero for ions with 54 and 68 electrons. Both these numbers of electrons are capable of forming "completed configurations" in the previously discussed sense (see Table V)—54 corresponding to X, and 68 to X with 14 more electrons filling up the N VI(6) and N VII(8) levels. The curve consists of two unequal portions, so that the energy difference between the two sets of levels must be sufficiently marked for the first to be partially completed before the upbuilding of the second begins. (In the first transition series there is no indication that two separate levels (M IV and M V) are involved.) The magnetic moment of Gd^3 according to the measurements of Onnes is 39·2, which corresponds very closely to 7 Bohr magnetons. This is rather striking, as Gd^3 with 61 electrons contains 7 more electrons than the completed 54 configuration. In general the moment, in Bohr units, does not exceed the number of electrons the ion contains in excess of 54.

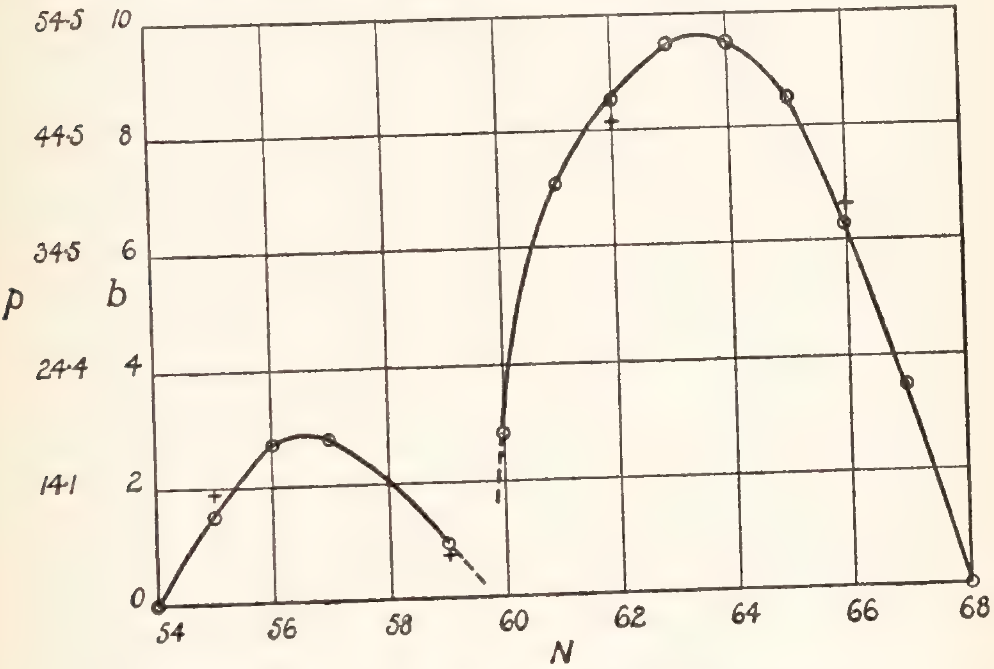


FIG. 31.—Ionic Magnetic Moments of Rare-earth Elements.

The ratio of the maximum value of $(\bar{\mu}/\mu)$ to the initial slope of the $(\bar{\mu}/\mu,\ a)$ curve according to Pauli's treatment would be $\frac{6b^2}{(b+1)(2b+1)}$, and according to Sommerfeld's $\frac{3b}{b+2}$ (cf. Table VI, Ch. V). For $b = 7$, these expressions are equal to

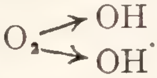
2·45 and 2·33, so both are compatible with the observed fact that for gadolinium sulphate $\left(\frac{\bar{\mu}}{\mu}\right)_{\max} \nless 2{\cdot}12 \left(\frac{\bar{\mu}}{\mu a}\right)_0$.

The fascinating problems raised by the ionic moments of transition elements makes it desirable that the measurements should be extended as far as possible to members of other series, involving the elements Y–Pd, Ta–Pt, and U (Table III).

Gases.—The moments for O_2 and NO (14·16 and 9·20) are calculated on the basis of the implicit assumption that the molecules are rigid, and have a single elementary magnetic carrier. The molecular specific heat of oxygen (4·98 at 20° C., 4·91 at − 180° C.) is in agreement with this view, and is usually taken to indicate that the molecule has five degrees of freedom, three translational and two rotational. Expressed in terms of Weiss units the numbers for the moments diverge far more widely from integers than can possibly be accounted for by experimental error. If it is assumed that two carriers can exist in the molecules, each free to orientate independently, then whole numbers can be obtained. Putting $p^2 = p_1{}^2 + p_2{}^2$ (VI, 3), for oxygen $p_1 = p_2 = 10$ fits the results; for NO the values 9 and 2, or 7 and 6; but the Weiss magneton is not to be upheld in this manner.

The quantum orientation interpretation of magnetic moments was first put forward by Pauli (1920) and was applied by him to these two paramagnetic gases; and the fact that the numbers agree so closely with those corresponding to 1 and 2 Bohr magnetons (Table XIX) can hardly be regarded as fortuitous. The agreement is far from exact, the numbers calculated by Pauli for 1 and 2 quantum orbits differing by 7 per cent. and 4 per cent. from those actually observed; but, as for the paramagnetic ions, there can be little doubt that the basis of the quantum treatment is correct. The oxygen p value, moreover, does agree very closely with that calculated by Sommerfeld for $b = 2$ (corresponding to a "triplet" atom in an s state).

The question as to the actual nature of the carriers raises the chemical problem of the structure of the NO and O_2 molecules. NO is one of the few "odd" molecules, having a total of 15 electrons. Of these presumably four constitute two pairs of K electrons round the two nuclei, but the extent to which the orbits of the rest are "shared" is, at present, a matter of pure speculation. One electron, however, does seem to be differentiated, and the whole NO molecule behaves to a certain extent as if it possessed a valence electron like the alkali metal atoms, though the relative weakness in the binding of the "valence" electron is not so marked. The possession of a valence electron is shown by the formation of compounds such as NOCl, NOF and NO.OH. Now the Zeeman effect, and the Gerlach and Stern experiments show that the valence electron orbit in alkali-like atoms does take up a definite orientation in an applied field, though whether the whole atom orientates with it (as a rigid whole) is unknown. The NO molecule probably behaves in a similar manner. The valence electron orbit tends to orientate in the field, and if it is relatively free as regards orientation with respect to the rest of the molecule, it may tend to preserve the stable orientation in spite of molecular rotation, and intermolecular collision. Divergences of the observed magnetic moment from that calculated in any simple manner would certainly be expected! The picture raises many difficulties, but it seems not unreasonable, in view of its harmony with other evidence; and the magnetic properties of the NO molecule may be tentatively attributed to its possessing one "unbalanced" electronic orbit with a moment corresponding to one Bohr magneton.

Oxygen is rather more complicated. The molecule has an even number of electrons, but these do not balance magnetically. Chemically it is possible to differentiate two of them. Representing the twelve electrons (those in excess of the K electrons) by dots, Lewis represents O_2 not only as $:\ddot{O}::\ddot{O}:$, with four "shared" electrons, but also as $:\underset{\cdot}{\ddot{O}}:\underset{\cdot}{\ddot{O}}:$ with only two. Just as the one electron external to a system of 10 in NO behaved as a valence electron, so do the two—but less pronouncedly—in oxygen. Ozone may be regarded as $O_2 \rightrightarrows O$, and Bach's ozonic acid as  $O_2\begin{smallmatrix}\nearrow OH\\ \searrow OH\end{smallmatrix}$. In the possession of two electrons external to a closed system, the oxygen molecule has analogies with alkali-earth atoms. These atoms give rise to singlet and triplet spectra. For triplets, the atoms in the *s* state have two electrons external to a closed configuration both rotating in orbits for which $k = 1$; and the maximum magnetic moment (with the electrons rotating in the same sense) corresponds to $b = 2$. It is for such atoms that Sommerfeld's calculation yields a p value of 14·1. The difficulties in connection with the freedom of the two electron orbits relative to the rest of the oxygen molecule are similar to those for NO; but the moment observed for the oxygen molecule (both in the gas and the liquid) give the strongest support for the validity of the quantum magneton-orientation hypothesis.

The moments observed for paramagnetic ions in solids agree approximately with those for the ions in solution. The susceptibility of solid oxygen, on the other hand, shows striking peculiarities (Fig. 27), that for one modification actually decreasing with decrease in temperature. Onnes has suggested that some form of magnetic "congelation" occurs. This "congelation" can, however, be given a by no means recondite interpretation. The pair of electron orbits, magnetically mobile so long as the molecules persist as individuals, constitute relatively immobile shared binding links in the structure of the crystalline edifice. Stronger forces (of the unknown type of those which maintain the quantum electronic orbits in an atom in equilibrium) intervene, and interfere with the tendency to reorientation; these forces are more effective the lower the temperature. While increase of temperature will be accompanied by increase in freedom to reorientate, the thermal motions tend to disturb the magnetic equilibrium more and more. There is thus a possibility of accounting qualitatively for either a decrease or an increase in the paramagnetic susceptibility. Here the "magnetic" electrons are also binding electrons in the crystal structure; in the paramagnetic solid salts, the binding electrons are independent of those which give the ion its magnetic properties.

It would be of great interest if the magnetic properties of ozone, which is said to have a high specific paramagnetic susceptibility (Becquerel, 1888), could be carefully investigated. A fundamental mode of attack on the magnetic problems raised by O_2 and NO as gases must, moreover, undoubtedly be sought in the study of the molecular spectra. A considerable number of bands have been measured, but with the data uncorrelated, and the interpretation uncertain, discussion would as yet be unfruitful for the present purpose.

Ferromagnetics.—The deduction of elementary moment values from the measurements on ferromagnetics (and other elements obeying a Weiss law) is very uncertain; above the Curie point the results yield the root mean square value of the moment per atom; saturation gives the arithmetic mean value per atom; and it is only if the atoms all contain similar carriers that the moment so deduced is significant. The crystal lattice is probably built up of ions not all having the same number of electrons; stability conditions may involve an actual mutual transfer of electrons, while some of the electrons may be shared. No simple quantum calculation would be expected to give a close approximation to the results, even if the ionic constitution of repeated groups in the crystal was known, and the effective magnetic parts of the ions were relatively free to orientate. A short discussion may, however, be given, rather indicating tentative points of view which may suggest lines of attack on the problems. It will be assumed from now onwards that the Weiss magneton has no physical existence, the p values simply serving as a measure of the moments.

Iron, cobalt and nickel, like most of the metals, have a simple crystalline structure, which is probably connected with the similarity in size of the ions. At room temperature iron is body-centred cubic ($d = 2{\cdot}87$ A.U.), nickel face-centred ($d = 3{\cdot}52$), cobalt hexagonal ($a = 2{\cdot}514$, $c = 4{\cdot}105$), and also possibly face-centred ($d = 3{\cdot}55$). Seventy per cent. of the Ni may be replaced by Fe without change in its structure; while the alloys with $0 - 25$ per cent. Ni retain the Fe structure. Fe-Co alloys remain body-centred with up to 80 per cent. Co; with 90–98 per cent. Co the predominant structure is face-centred; with more Co the hexagonal structure appears. These changes are to a certain extent reflected in the low-temperature saturation curves (Fig. 29).

If the saturation moments observed are interpreted as characteristic of groups of atoms, they do not seem incompatible with a distribution of integral numbers of Bohr magnetons among the ions. More than this cannot be said, but a few examples may be given. For Fe_3Ni_2, $p = 45$ or $b = 9$. The group of five atoms in a crystal structure which is the same as that characteristic of nickel suggests taking $p = 15$ for Ni_5 (or $b = 3$) and $p = 55$ ($b = 11$) for Fe_5. The Fe-Co curve gives $b = 2$ per atom for Fe, so that molecular groupings compatible with whole numbers are not restricted; for Fe_2Co, p differs little from 35 ($b = 7$); for Co_5, $b = 9$.

Above the Curie point somewhat similar considerations may apply. If p_A is the deduced moment per atom (see Table XVII), then for a group of n atoms, $p^2 = n^2 p_A{}^2$; and p^2 may be regarded as the sum of contributions $p_1{}^2 + p_2{}^2 \ldots$ from the magnetically independent ions. It is then generally possible to account for the observed p_A by making an assumption as to n, and an assignment of values for $p_1, p_2 \ldots$ from Table XIX. Until the appropriate quantum p values corresponding to higher values of b are more certainly known, however, and as there is no independent evidence as to the molecular groups, it does not seem desirable to speculate too wildly. For Ni, between 412° and 900°, $p_A = 8{\cdot}02$, giving for Ni_5 $p^2 = 5 \times (8{\cdot}02)^2 \doteq 320$; the values $p_1 = 16$ (that observed for Ni^2), $p_2 = 8{\cdot}6$, $p_3 = p_4 = p_5 = 0$, give $p^2 = 330$. This suggests that the magnetic behaviour of nickel both at low and high temperatures can be approximately accounted for on the same assumption—that among every 5 atoms there is one carrier with 2 and one with

1 Bohr magneton ; and that there is no marked magnetic change of state in the nickel between the lowest temperatures and the Curie point, which accords with the fact that there is no discontinuity in the saturation intensity—temperature curve. The Weiss view necessitates the supposition that there is a gradual change in the equilibrium between two types of nickel, one with 3 and the other with 8 Weiss magnetons per atom.

The moment of iron above the Curie point does not seem explicable on the assumption that the carriers are the same as those at low temperatures. The changes in the slope of the $\left(\frac{1}{\chi}, T\right)$ curves indicate a change in the moments of the carriers, due presumably to changes in the electronic constitution of the ions ; the magnetic change from β to γ and γ to δ iron is accompanied by a change in crystal structure, γ iron, at about 1,000°, being face-centred ($d = 3{\cdot}60$), α, β and δ iron being body-centred ; the crystal structure of β_1 and β_2 iron is apparently the same (see Table XVII).

The only other elements following a Weiss law that have been carefully investigated are Pd and Pt (Table XV), and it is interesting that both of these, occupying a position in the periodic table similar to that of nickel, have the same predominant magnetic moment ($p_A \doteqdot 8$). The crystal structure is also the same (face-centred).

While the ferromagnetic moments do not lend themselves readily to a quantum interpretation, they cannot, in the present state of knowledge, be regarded as invalidating the quantum ideas ; rather the general quantum magneton theory seems extraordinarily useful in suggesting lines of attack on the many problems which ferromagnetics present. The consideration of paramagnetic elements not following a Weiss law will be reserved until intrinsic fields have been further discussed.

3. Intrinsic Fields

Weiss's Molecular Field.—According to Weiss's theory, the behaviour of substances which follow the law $\chi = \frac{C}{T - \theta}$ may be accounted for on the assumption that there is a molecular field, which, although almost certainly not magnetic in origin, may be treated as magnetic, and is proportional to the intensity of magnetization acquired. Writing $H_i = NI$ for the internal field, N and θ are related by the equation (IV, 28)—

$$\theta = \frac{\sigma_{m_0}{}^2 N \varrho}{3mR}$$

σ_{m_0} being the saturation moment per gram molecule, ϱ the density, m the molecular weight.

$$N = \frac{3mR\theta}{\sigma_{m_0}{}^2\varrho} = \frac{m\theta}{C_M\varrho} = \frac{\theta}{C\varrho} \quad . \quad . \quad . \quad . \quad (5)$$

Approximately, expressing σ_{m_0} in Weiss magnetons,

$$N = 198\frac{m\theta}{\varrho p^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5{\cdot}1)$$

The internal field is then given by

$$H_i = NI = 198\,\frac{m\theta}{p^2}\left(\frac{I}{\varrho}\right) \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Calculating N from the data of Table XVII, values of the order of $3{\cdot}4 \times 10^3$, $8{\cdot}6 \times 10^3$ and 14×10^3 are obtained for Fe, Co and Ni respectively (corresponding to maximum fields, when the metals are saturated at ordinary temperatures, of the order of $5{\cdot}8 \times 10^6$, 11×10^6 and $7{\cdot}6 \times 10^6$ "gauss").

For Ni-Co alloys, writing C_{Ni} and C_{Co} for the fractional molecular concentration of the Ni and Co,

$$N = (13{\cdot}8\,C_{Ni} + 8{\cdot}6\,C_{Co}) \times 10^3$$

As has already been discussed (Ch. IV, sect. 4) this led Weiss to the conclusion that in a binary alloy in which only one of the metals was ferromagnetic N would be proportional to the density of the ferromagnetic metal, which suggested an inverse sixth-power law for the variation of the internal field with distance from the elementary magnets. For mixtures of liquid oxygen and nitrogen, however (Ch. VI, sect. 5), θ varies directly as the concentration of the oxygen, so that N is independent of this ($N \doteqdot -1{\cdot}27 \times 10^3$). With similar reasoning, this would suggest an inverse cube law, which is that required by the view that the molecular field is electrostatic in origin, arising from the magnetic carriers also being electric dipoles. As this would lead to a positive field, however, and θ is negative for the oxygen-nitrogen mixtures, the conclusion which may be drawn is that the molecular field cannot be interpreted as being simply either magnetic or electrostatic; and that the forces cannot be supposed to follow any unique law of variation with distance from the magnetic carriers.

That there are strong forces of some kind, whose effects are similar to those of magnetic fields, is undoubted; for otherwise it is impossible, either on the basis of the classical Langevin theory or its modification resulting from the consideration of discrete orientations, to account for the attainment of saturation of ferromagnetics in relatively weak fields, or for the low susceptibilities of substances with a negative value of θ. It is therefore somewhat surprising that these fields should not have been placed more strongly in evidence by the experiments on ferromagnetic crystals (Ch. VI, sect. 6). Webster has deduced from his work on iron crystals molecular fields of the order of only a few hundred gauss. This interpretation of the results is, however, rather due to the use of the term "molecular field" in a sense which is different from the usual one. From the fact that saturation may be obtained readily, there must be large molecular fields proportional to the intensity of magnetization. Directly, the experiments only give the intensity in magnitude and direction for the fields applied; this may differ for different directions of application of the field. For the iron crystals the intensity for any direction of application of the field (if this is not very small) is far in excess of that which a normal paramagnetic would acquire, so that the value of N must be large for every direction in the crystal. Any variation in $I_{\parallel}$ or $I_{\perp}$ with direction indicates that N is not the same for all directions; and the way in which the molecular field was calculated gives not NI but an estimate of the maximum value of $I\delta N$, δN being the difference in N along different directions. For iron crystals N is approximately the same in all directions; the experiments only indicated relatively small variations for a narrow range of applied field magnitudes, when the intensity was somewhat smaller along the diagonals than along the quaternary crystal axes.

In pyrrhotite the value of N differs markedly along axes at right angles in the elementary crystals; there is a magnetic plane and a direction of easy magnetization; and the existence of strong internal fields is clearly shown because $I\delta N$ may be large.

In the two discs studied by Webster the resultant molecular field was 620 and 470 gauss. The difference was attributed to impurities, whose effect was apparently very large; the fractional changes in N required to produce this resultant change in $I\delta N$ will, however, be quite small, and quite of the order which might be anticipated from the distortion in crystal structure which small quantities of impurity may produce.

Broadly speaking, the work on ferromagnetic crystals confirms Weiss's theory; and the important fact emerges that N is a function of direction in the crystal. The work on iron crystals, however, in showing that these do not possess a favoured direction of easy magnetization, indicates that Weiss's general theory of ferromagnetics (Ch. IV, sect. 3) is based on assumptions which are far too simple; for the elementary crystals orientated at random in an ordinary piece of iron are capable of acquiring saturation intensities in any direction, though the single crystal results show that they will not do so under the influence of very small applied fields. A single crystal may be magnetically neutral. (It may be noted, in the light of the discussion on Ewing's theory, that this is possible even if there are favoured directions of easy magnetization, provided that these are not all parallel.) It seems as if the very varied hysteresis phenomena observed are to be explained largely by the differences in the magnitudes of the external fields which must be applied to the individual crystals, in order that the field direction may become a favoured one for the occurrence of saturation. The external field has to overcome the internal molecular fields which are not uniformly directed but tend to keep the crystal in a quasi-stable neutral state; the crystal eventually assumes another quasi-stable magnetized state. Even if a comparatively small field is necessary to bring about the transition, the applied field may have to be large owing to the high value of the demagnetizing field, particularly when the crystals are small. This view is to a certain extent confirmed by the work on thin films (Ch. VI, sect. 6).

That ferromagnetism is a property of the crystal aggregate, and not of the individual atom, is strongly supported by the experiments of Ingersoll and Vinney on thin films of nickel.

Though the problems presented by ferromagnetics, which group themselves round the molecular field theory, are far from being solved, the lines along which successful attacks may be made on them seem fairly clearly indicated. The experimental study of single crystals is in its infancy; the difficulties, though considerable, are not insuperable. There is room for much more work on the magnetization curves of the ordinary substances, consisting of aggregates of small crystals, particularly if carried out in conjunction with investigations on the crystal grain sizes by the X-ray methods now available. Further, the information to be gained from the study of thin films is by no means exhausted.

Paramagnetic Crystals. Foēx's Theory.—In a crystal it is not unreasonable to suppose that the magnetic carriers tend to take up a definite orientation distribution, the potential energy of a carrier being a function of its orientation with respect to the crystal axes. This view was put forward by Weiss. Foëx has attempted to develop a general theory of paramagnetic crystals by taking into account both this intrinsic crystalline field, and the Weiss molecular field proportional to the intensity. The theory, though purely qualitative, may be briefly sketched, as it is very suggestive in connection with some of the low-temperature work.

Taking Langevin's expression in the form appropriate for small fields (cf. IV, 15 and 16),

$$\sigma/\sigma_0 = (\sigma_0 \mathrm{H}/\mathrm{RT})\,\overline{\cos^2\theta} \quad . \quad . \quad . \quad . \quad . \quad . \tag{7}$$

$$\sigma = (3\mathrm{CH}/\mathrm{T})\,\overline{\cos^2\theta} \quad . \quad . \quad . \quad . \quad . \tag{7.1}$$

σ being the intensity of magnetization, C Curie's constant, $\overline{\cos^2\theta}$ the spatial mean value for limitingly small fields, and θ the orientation of the elementary magnet with respect to the field. If there is a potential energy W for each orientation, then

$$y = \overline{\cos^2\theta} = \int e^{-\frac{\mathrm{W}}{\mathrm{RT}}}\cos^2\theta d\omega \Big/ \int e^{-\frac{\mathrm{W}}{\mathrm{RT}}} d\omega \quad . \quad . \quad . \tag{8}$$

In a crystal y may be supposed to have different values y_1, y_2, y_3 for the three principal directions; introducing also a Weiss molecular field, with constants n_1, n_2, n_3, where $n = \mathrm{N}\varrho$, (7.1) becomes

$$\sigma_1 = \frac{3\mathrm{C}}{\mathrm{T}}(\mathrm{H} + n_1\sigma_1)y_1 \quad . \quad . \quad . \quad . \quad . \quad . \tag{9}$$

with corresponding expressions for σ_2 and σ_3.

For the principal susceptibilities

$$\chi_1 = \sigma_1/\mathrm{H} = 3\mathrm{C}y_1/(\mathrm{T} - 3n_1\mathrm{C}y_1) \quad . \quad . \quad . \tag{9.1}$$

$$\frac{1}{\chi_1} = \frac{\mathrm{T}}{3\mathrm{C}y_1} - n_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \tag{9.2}$$

If in (8) W = 0—there is no potential energy of orientation—$y_1 = \frac{1}{3}$, and (9.2) reduces to the Weiss expression

$$\frac{1}{\chi_1} = \frac{\mathrm{T}}{\mathrm{C}} - n_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \tag{9.3}$$

(9.2) therefore indicates departures from the Weiss law, whose nature can only be determined by making specific assumptions as to the variation of y with temperature; the deviations will be most marked at low temperatures, while at high temperatures, when RT becomes large, the Weiss law will be asymptotically followed.

It may be noticed that if the molecular field is zero, the mean susceptibility, which is measured with powders, will obey the Curie law—

$$\bar{\chi} = \tfrac{1}{3}(\chi_1 + \chi_2 + \chi_3) = \frac{C}{T}(y_1 + y_2 + y_3) = \frac{C}{T} \quad . \quad (10)$$

(This follows from 8, for $\Sigma \cos^2 \theta = 1$ for three directions at right angles.) Also for a regular cubic crystal, the principal susceptibilities are equal—

$$y_1 = y_2 = y_3 = \tfrac{1}{3} \qquad n_1 = n_2 = n_3 = n$$

$$\chi_1 = \chi_2 = \chi_3 = \bar{\chi} = \frac{C}{T - nC} \quad . \quad . \quad . \quad (10.1)$$

and a Weiss (or Curie) law will be followed.

Foëx supposes that at absolute zero y may have values varying from 0 to 1; and he considers the nature of the $\left(\frac{1}{\chi}, T\right)$ curve which would result if y approached its high-temperature value of $\frac{1}{3}$ in the two typical ways represented by the curves (a) and (b) of Fig. 32. The general form of the $\left(\frac{1}{\chi}, T\right)$ curves are shown in ($a1$) and ($a2$) and ($b1$) and ($b2$), the asymptotic Weiss curves (equation 9.3) being dotted.

For $T = 0$, $\frac{1}{\chi} = -n$, giving the point of intersection on the $\frac{1}{\chi}$ axis; while $\frac{1}{\chi} = 0$ for $T = 3\,Cyn = \theta'$. θ' will differ from the value $\theta = Cn$ given by extrapolation of the Weiss curve. The curves of Fig. 32 are all drawn for n negative; those for n positive will be similar, but displaced parallel to the $\frac{1}{\chi}$ axis so that the T axis is intercepted for a positive value of T. The curves of Fig. 32 differ from those given by Foëx, who states that asymptotically (when $y = \frac{1}{3}$) they will be *parallel* to the Weiss line, while it is clear from (9.2) and (9.3) that they will coincide with it. In view of this, Foëx's comparison of theoretical and experimental curves will not be examined in detail; on the whole the curves of Fig. 32 agree less closely with those observed, but the way in which some of the peculiarities of the experimental curves (such as those of Jackson—Fig. 28) are qualitatively reproduced is very striking and worthy of note. According as y is greater or less than $\frac{1}{3}$, the $\left(\frac{1}{\chi}, T\right)$ curve lies wholly below or above the Weiss line. Various types of curvature are possible; maxima and minima can appear if y is less than $\frac{1}{3}$, and varies with temperature in the manner shown in Fig. 32 (*b*). (Fig. 32 (*b*1).)

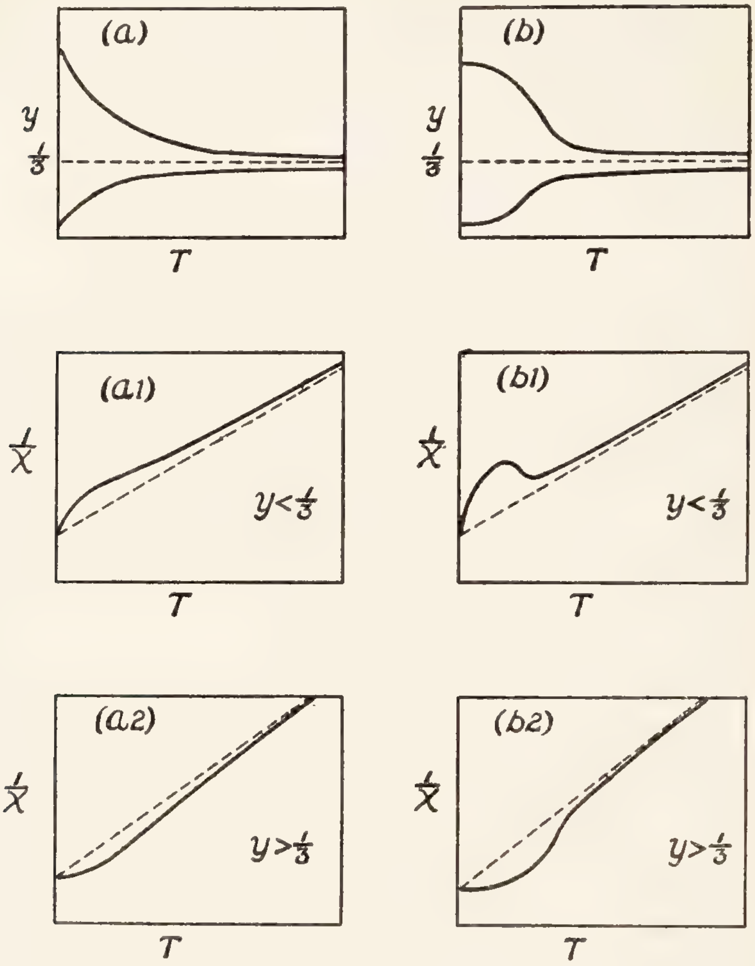


FIG. 32.

(*a*1), (*a*2) and (*b*1), (*b*2) represent theoretical types of $\left(\frac{1}{\chi}, \mathrm{T}\right)$ curves for n negative, corresponding to variations in y shown in (*a*) and (*b*).

There are one or two consequences of the theory which do not seem to have been sufficiently emphasized. If y tends to $\frac{1}{3}$ at high temperatures, then points on the corresponding Weiss curve (9.2) are given by the high-temperature measurements, and by the (extrapolated) point of intersection of the $\left(\frac{1}{\chi}, \mathrm{T}\right)$ curve with the $\frac{1}{\chi}$ axis ($\mathrm{T} = 0$); and the magneton value for the carrier would more appropriately be deduced from the line through these points than from the straight portions of the observed curve. While the theory is in too qualitative a form and the low-temperature data are too scanty to make it worth while to examine in detail the results of this at present, one important point emerges. If there is a potential energy of orientation, then the slope of the $\left(\frac{1}{\chi}, T\right)$ curve given by (9.2) will depend on the value of y over the range of temperature considered; and the deduced magneton value p' for the carrier will differ from the true value p in such a way that $p'/p = \sqrt{3y}$. The fact that different magneton values are found for the same carrier may possibly be partly accounted for in this way.

Quantum Considerations.—No quantum ideas enter into Foëx's theory. It is Langevin's theory modified and extended by the introduction of "molecular" and "crystalline" fields. The quantum theory supposes that only certain discrete orientations of the magnetic carriers are possible in an external magnetic field. (So that, in equation 8, for $b = 1$, for example, $y = 1$; giving the results for elementary moments already discussed.) The results obtained on the magneton-orientation hypothesis in its simple form will only hold if the carriers are controlled as regards their settings solely by the external field, and if they are free to reorientate themselves with respect to it. The possible orientations are fixed even in a limitingly small field; but a resultant magnetic moment is only acquired if, under the influence of fields of increasing magnitude, a redistribution of the carriers among the different possible settings can take place. The final distribution depends jointly on the temperature (the intrinsic thermal radiation is probably the main agent involved) and the field strength (which determines the energy difference between different orientations).

The moments deduced for paramagnetic ions in solution or in solid salts are in sufficient agreement with those calculated to show that the conditions are at least approximately fulfilled. This does not mean that the carriers persist indefinitely, rigidly poised in space, unshaken by any disturbance; but simply that the time occupied by transitions between different stationary states, brought about by collisions, or emission or absorption of radiation, is small compared with the time occupied in the stationary states.

The crystalline form of solids must be supposed to depend primarily on the outer electrons of the constituent atoms; it is these which form the binding links in the structure. Crudely, a paramagnetic salt crystal may be regarded as a comparatively stable structure built up of outer electrons of the atoms; this structure being full of "holes" in which are the actual ions, free to change their orientation. Magnetization would not be expected to affect the crystal structure, in agreement with the fact that all experiments to detect such changes, such as those of Compton and Rognley, have given a negative result.

The difficulties in connection with NO and O_2 have been discussed, and it was suggested that the magnetic electrons might be relatively free with respect to the rest of the molecule; it must be admitted, however, that it seems extraordinarily difficult to conceive of a stable molecule in which one or two electron orbits can take up stationary orientations, while the rest of the molecule rotates vigorously about equatorial axes! For it is improbable that the magnetic electron orbits are wholly external to the remainder of the molecular electrons. O_2 and NO remain mysterious!

Returning to solids, there will be in a crystal, even in the absence of an external field, definite directions which will form lines of reference for spatial quantization. The orientation of orbits generally seems to be governed rather by symmetry conditions than by the exact nature of the fields defining directions. Just as, for some reason inexplicable on a purely electromagnetic basis, only certain orbits are possible, so are certain definite orientations possible. The statement that quantum orientations depend on symmetry conditions is therefore wider, but less fundamental than the statement that they depend on resultant field directions; for it implies that other factors may enter which hitherto have not been explained on a field theory. In a crystal, however, lines of symmetry and resultant field directions will be closely related.

In a crystal, free carriers may be supposed to orientate themselves in definite directions relative to axes of symmetry. As the crystals are unmagnetized in the absence of an external field, the resultant intrinsic magnetic field in the crystal corresponding to any favoured direction must be non-uniform as to sense—it must be as frequently negative as positive. The application of an external magnetic field defines a new direction, and if this field is strong compared with any residual fields in the crystal, the carriers will orientate themselves relative to it in accordance with quantum rules; otherwise they will orientate themselves relative to directions which will be determined by the resultants of the external and the internal fields. These purely tentative suggestions indicate the possibility of a quantum modification of the Foëx theory, and so of a quantum explanation of some of the peculiarities of the $\left(\frac{1}{\chi}, T\right)$ curves, and of the observed variations in the magneton numbers.

Changes in orientation of the ions will have a distorting effect on the "stable" structure built up by the external electrons of the atoms; the fields due to these may be modified in such a way as to increase or decrease the intensity of magnetization acquired. It is imagined that the Weiss molecular field arises in this manner. The molecular field will then be a function of the intensity of magnetization, but as the effect is an indirect one, neither the sign nor the magnitude of the coefficients can be calculated a priori from any simple magnetic considerations. The field in a small region of a crystal is regarded as arising partly from the carriers, and partly from the remainder of the structure; a change in orientation of one of the carriers will induce a change in the "structure field"; and this may be in a sense to oppose similar reorientations of other carriers (of a diamagnetic nature) or to help them (of a paramagnetic nature). The fields involved will be those in the immediate neighbourhood of electronic orbits and not at interatomic distances, and so may readily be of the order of magnitude required. (See Ch. V, sect. 3 for numerical data.) It is in this connection that Ewing's later views are of interest (Ch. IV, sect. 1). Quantitative advances along these lines require much more detailed knowledge of crystal structure. There is a fascinating problem as to why large positive molecular fields appear for iron, cobalt and nickel; molecular fields being in general either small or negative. In framing more complete theories this must be borne in mind; as also the facts that there is *some* relation between the molecular field and the magnetic dilution, and the apparent magneton values deduced for the carriers.

Anomalous Paramagnetism.—The behaviour of many paramagnetic elements (Table XIV) is peculiar in that the susceptibility may remain constant or even increase with temperature; a constant paramagnetism is also shown by potassium permanganate, and potassium bichromate in solution, as already mentioned. In all such cases the atomic or ionic susceptibility is much smaller than that of typical paramagnetics following a Weiss or a Curie law. The general nature of the explanation which may be given will be clear from the discussion on solid oxygen and that on intrinsic fields. If paramagnetic atoms unite into a crystal structure, they will only be able to show typical paramagnetic behaviour if the carriers are free to change their orientation; and this will be impossible if the magnetic electron orbits form the binding links which build up the stable crystal structure, for the crystalline forces, whatever their nature, are then enormous compared with those which can be applied artificially. At low temperatures, the atoms, and the associated magnetic orbits, become less and less mobile. Increasing temperature, resulting in increasing freedom, allows the magnetic orbits to change their orientation under the influence of a field to a greater extent, and there may actually be an increase in the paramagnetic susceptibility; at the same time the temperature effect becomes more important in disturbing the equilibrium distribution, which would be taken up under the influence of the field alone. An increasing, decreasing or constant susceptibility will therefore be observed according to the predominating effect. The anomalous paramagnetics offer a promising field for further research, which might shed much light on many obscure problems.

REFERENCES. VII

General

Most of the references given at the end of the last chapter apply here also, the papers of Weiss, Foëx and Jackson being particularly valuable.

Sommerfeld gives an excellent brief account of quantum-magneton theory (*Atombau*, Ch. VIII, sect. 4, "Zur Theorie des Magnetons") with full references.

The more important original papers on the magneton-orientation hypothesis are:

PAULI. "Quantentheorie und Magneton," *Phys. Zeit.* 21, 615 (1920).
EPSTEIN. *Science*, 57, No. 1479 (1923).
GERLACH. *Phys. Zeit.* 24, 275 (1923).
SOMMERFELD. "Zur Theorie des Magnetons," *Zeit. f. Phys.* 19, 221 (1923). (1)

For ionic magnetic moments, in addition to the sources already given, see—

DORFMANN. "Magnetonenzahlen und Atombau," *Zeit. f. Phys.* 28, 286 (1924).
ST. MEYER. "Magnetisierungszahlen seltener Erden," *Phys. Zeit.* 26, 51 (1925).
WEISS. "Les moments atomiques des terres rares d'après B. Cabrera," *Journ. de Phys.*, Bull. 218, p. 86S (5 June, 1925).

The chemical side of the oxygen and nitric oxide problem is interestingly discussed by—

LEWIS. *Valence and the Structure of Atoms and Molecules*, Amer. Chem. Soc. Monograph Series. (New York, 1923.)

Fairly complete data on the crystal structure of ferromagnetic metals and alloys, and a brief discussion on the connection with magnetic properties, are given by—

Wyckoff. *The Structure of Crystals.* Amer. Chem. Soc. (New York, 1924.)

Weiss. " Equation d'état et variation du moment atomique," *Comptes Rendus,* 180, 358 (1925).

Foëx. " Les divers états magnétiques d'un ion," *C.R.* 180, 919 (1925). (2)

Debye (*l.c.*) gives an excellent discussion of the molecular field ; the papers of Weiss (*l.c.* Ch. IV) should also be consulted. Theories of ferromagnetic crystals are summarized by Kunz (*B.N.R.C.*). For the paramagnetic crystal theories, see Foëx, *l.c.* Quantum considerations do not seem to have been applied to intrinsic field problems. Anomalous paramagnetism is briefly discussed by Weiss and Collet (*l.c.* Ch. VI).

CHAPTER VIII

THE GYROMAGNETIC EFFECT

1. Theory

SINCE the elementary magnets consist of electrons, possessing inertia, rotating in orbits, the elementary magnetic moments will always be associated with mechanical moments. This suggests the possibility of gyromagnetic effects for matter in bulk—that magnetization may be accompanied by rotation and rotation by magnetization. A theory was first given from a modern electronic standpoint by O. W. Richardson (1908), and has been developed by S. J. Barnett (1909), Schuster (1912), Einstein and de Haas (1915) and others. The theory will first be stated in the simplest possible manner.

Section 7 of Chapter II, and 3 of Chapter V, should be consulted. Let $\boldsymbol{\mu}$ be the magnetic moment of an orbital electron, $\mathbf{j}$ the angular momentum (mechanical moment). Then (II, 60)

$$\boldsymbol{\mu} = \frac{e}{2mc}\mathbf{j} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\frac{\mathbf{j}}{\boldsymbol{\mu}} = \mathrm{R} = \frac{2mc}{e} = -1{\cdot}13 \times 10^{-7} \quad . \quad . \quad . \quad (1.1)$$

In paramagnetics, magnetization consists essentially in the alignment of the elementary magnets originally orientated at random. The total resultant angular momentum of the carriers will be related to the total resultant momentum by (1.1). The orientation does not occur directly under the influence of the field (Ch. IV, sects. 2 and 4) but only as the result of interactions between the molecules. In a solid, the gain by the carriers of a resultant angular momentum must be accompanied by a loss of angular momentum by the remainder of the structure; the solid as a whole, on magnetization, must acquire an angular momentum of reaction which stands in the same ratio to the magnetization as that of the elementary mechanical to the magnetic moment but is opposite in sign. It may be said at once that as far as sign is concerned this is supported by experiment, assuming that the charges are negative. According to this presentation, if a rod is magnetized, and acquires a moment M, it simultaneously acquires an angular momentum J such that

$$J = -RM \qquad (1.2)$$

Conversely, if a rod is rotated as a whole, so that the angular momentum is J, the stable structure distinct from the magnetic carriers is primarily affected; the elementary magnets tend to maintain their axes fixed in space; this is equivalent to the carriers acquiring a resultant mechanical moment J relative to the rest of the rod, and hence, in virtue of (1.1), to the rod acquiring a magnetic moment M such that $M = J/R$.

The question will now be considered from a slightly different standpoint which is adopted by Debye. The couple $\mathbf{C}$ acting on any body is related to the change in its angular momentum by the (vector) equation

$$\mathbf{C} = \frac{d\mathbf{J}}{dt} \qquad (2)$$

If a rotation $\boldsymbol{\omega}$ is imposed on an elementary electron orbit magnet $(\boldsymbol{\mu}, \mathbf{j})$

$$d\mathbf{j} = \boldsymbol{\omega} \times \mathbf{j}\, dt \qquad (2.1)$$

The maintenance of the rotation involves the existence of a couple $\mathbf{c}$, such that

$$\mathbf{c} = \boldsymbol{\omega} \times \mathbf{j} \qquad (2.2)$$

with the opposite reaction, for electron orbits in a solid, on the solid as a whole. Now, for an elementary magnet in a field $\mathbf{H}$

$$\mathbf{c} = -\mathbf{H} \times \boldsymbol{\mu} \qquad (2.3)$$

Remembering the change of sign, therefore, the imposition on a solid of an angular velocity $\boldsymbol{\omega}$ is equivalent in its effects, on the carriers, and so on the magnetization of the solid, to the application of a magnetic field $\mathbf{H}$ such that

$$\mathbf{H} = \frac{j}{\mu}\boldsymbol{\omega} = R\boldsymbol{\omega} \qquad (2.4)$$

where $R = -1{\cdot}13 \times 10^{-7}$.

A similar conclusion is reached if the calculation is based directly on the Larmor precession theorem (II, 8 and 8.1), according to which the application of a field results in a precession of the electrons about the centre of force round which they move, with angular velocity $\mathbf{o}$.

$$\mathbf{o} = -\frac{e}{2mc}\mathbf{H} \qquad (3)$$

which, since, from (1), $\mu/j = e/2mc$, and reaction is concerned, is equivalent to (2.4).

The relation (1) will apply not only if the carriers have an intrinsic moment, but also if this moment is induced by a field, and (1.2) and (2.4) should hold for diamagnetics as well as for para- and ferro-magnetics. It is, however, only for ferromagnetics—essentially because these can acquire a large magnetic moment in a relatively weak field—that it is practicable to measure at all accurately experimentally the magnitudes of the quantities whose ratios are being determined.

It will be obvious that none of the treatments given, although they lead to the same results, have the satisfactory and inevitable character which is desirable. The problem is considerably more complicated than has been supposed, but before discussing it further, it will be convenient to consider the actual experiments which have been made, and the results to which they have led. Two types of experiments are suggested by the theory. In the first, based on (1.2), a small cylindrical rod is suspended by a fibre; it is magnetized suddenly, and the angular impulse turns the cylinder against the twist of the fibre. In the second, based on (2.4), a rod is rotated and the magnetization measured, and the field required to produce the same degree of magnetization in a stationary rod is then determined.

2. Chattock and Bates's Investigation

The investigation of Chattock and Bates on the gyromagnetic effect will be considered in most detail as it was carried out with great care, is direct, and seems most likely to be free from subsidiary sources of error. The method, the most straightforward one of the first type, had previously been used by Stewart. The apparatus is represented in Fig. 33.

The specimen, in the form of a wire some 10 cm. long and ·3 mm. diameter, was suspended by a delicate quartz fibre. The wire was magnetized by passing a current through the surrounding helix. The process of magnetization of the specimen must be complete in a time small compared with the free period of the suspended system, and a special key was employed enabling the current to be made and broken in a hundredth of a second. The current was made sufficiently large to give rise to residual magnetism (that is, to give the specimen a magnetization corresponding to a point on the upper practically horizontal portion of an I, H curve); a current was then passed in the opposite direction, the effect due to a reversal in the residual magnetism being examined. It is necessary to determine the magnetic

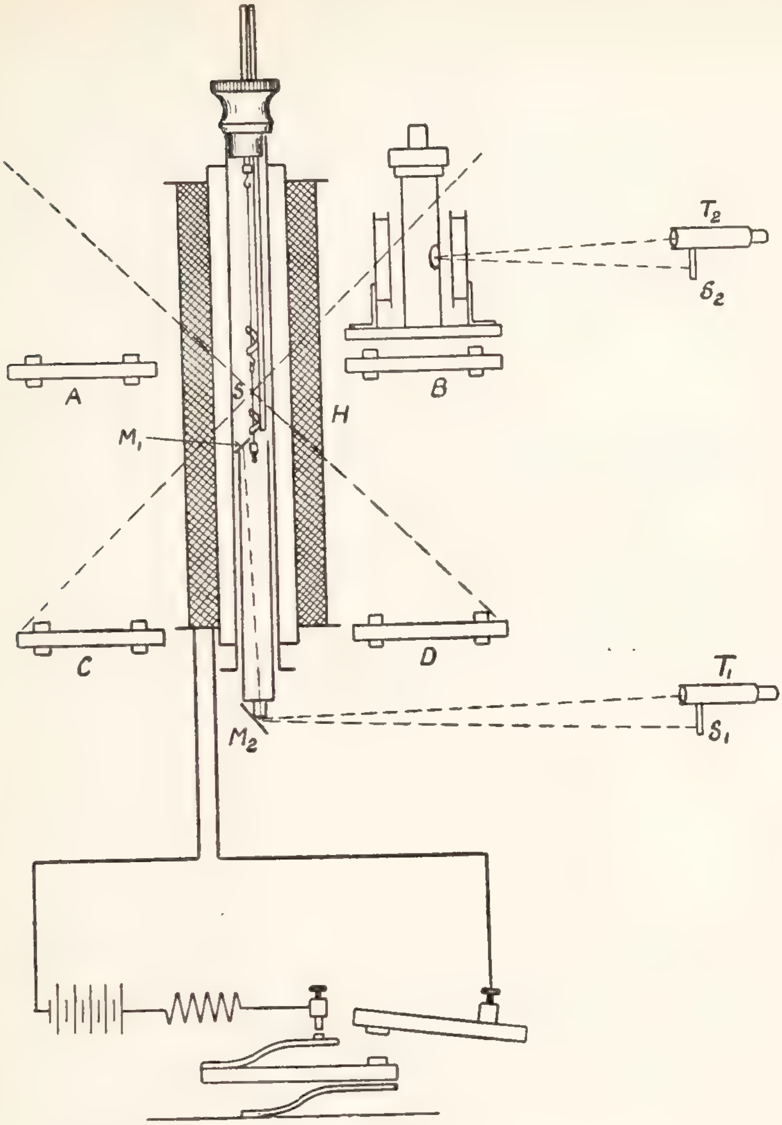


FIG. 33.—Chattock and Bates's Apparatus.

moment M of the specimen, and the angular momentum 2J resulting on its reversal.

The moment was measured by means of a suspended needle magnetometer which could be placed in any of the positions A, B, C, D. At the magnetometer needle

$$H = \frac{Md}{(d^2 - \frac{1}{2}l^2)^2} + \frac{M}{2(d^2 + \frac{1}{2}l^2)^{\frac{3}{2}}} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

d being the distance from the specimen to the needle, and l half of the effective length of the specimen.

($d \doteq 18$ cm.; $l = 4$ cm.); inserting the measured values (4) gave

$$H/M = 2{\cdot}663 \times 10^{-4} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.1)$$

The field due to the passage of a standardizing current passing through the magnetometer coils was found by the use of large subsidiary coils for which the constants could be readily determined; it was equal to $5{\cdot}768 \times 10^{-4}$ gauss; so that if ϕ_2 is the deflection due to reversal of the standardizing current and ϕ that due to reversal of a field H,

$$H = 5{\cdot}768 \times 10^{-4}\frac{\phi}{\phi_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.2)$$

Let ϕ_1 be the deflection due to a reversal in the magnetic moment of the specimen; then from (4.1) and (4.2)

$$M = 2{\cdot}166 \times \frac{\phi_1}{\phi_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.3)$$

Let I be the moment of inertia of the suspended system, ω the angular velocity resulting on magnetization, c the torsional constant of the suspending fibre, and θ_0 the throw, corrected for damping. Then

$$\tfrac{1}{2}I\omega^2 = \tfrac{1}{2}c\theta_0^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and

$$J = I\omega = \theta_0\sqrt{Ic} = \theta_0\frac{t_0 c}{2\pi} \quad . \quad . \quad . \quad . \quad . \quad (5.1)$$

In (5.1) t_0 is the (corrected) time of swing of the system. J is thus determined very simply from t_0, c and θ_0. In practice, however, θ_0 is very small, and the experimental difficulties come in the location and elimination of masking-effect errors.

The magnetic axis of the specimen is not necessarily vertical; the magnetic moment may have a small horizontal component m which will be acted on by any horizontal field f. Large coils were therefore set up to neutralize the earth's field. The horizontal moment m was reduced by changing slightly the tilt of the specimen. This was done by introducing a slight bend where the specimen was hung on the hook attached to the fibre. This junction was "stabilized" by a small quantity of paraffin wax. By supporting the specimen suitably—a rather elaborate "gallows" arrangement was used—the bend, and hence the tilt, could be adjusted by warming the wax. It was found that high symmetry was attainable and errors due to the earth's field could be practically entirely eliminated.

A second source of error may arise if there are horizontal fields due to the helix which are not parallel to any permanent or induced horizontal fields in the specimen. Many possible errors which might arise in this way are eliminated by taking means in the usual manner; and their magnitude may be estimated by magnetizing the specimen, and then putting on the helix current again in the same direction. Difficulties were further encountered in that pendulum-like vibrations may be induced, which give rise to disturbing oscillations. These could be largely overcome by tilting the helix.

A small mirror was attached to the specimen, a telescope and scale being used to measure the deflections, with two subsidiary mirrors inclined at 45° to the axis of the helix. The arrangement will be clear from Fig. 33.

The great patience required in experiments of this kind may be realized when it is noted that the order of magnitude of the deflections corresponding to the effect being measured was about 4 mm. scale divisions. Slight disturbances are sufficient to vitiate the results entirely, and in this work, which was carried out at Bristol, most of the actual experiments could only be made between 11.45 p.m. and 5.45 a.m.—when the trams were not running!

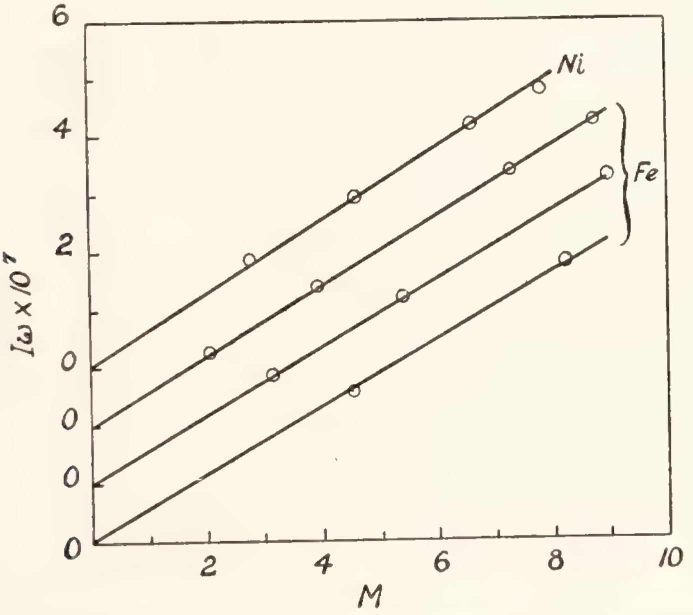


Fig. 34.—Relation between Magnetic Moment and Angular Momentum.

The results obtained for three wires of iron, and one of nickel, are plotted in Fig. 34, in which the numbers refer to the iron curves, and must be divided by five for the nickel.

A very definite proportionality is shown. As has already been mentioned the direction of the rotation corresponds to the reaction. If the rod is magnetized so that the north pole is uppermost (corresponding to electrons rotating in a clockwise direction) it turns (looking down on it from above) in an anti-clockwise direction. The values of the ratio deduced for J/M as a fraction of the theoretical value of $1{\cdot}13 \times 10^{-7}$ are given in the next table, with the number of determinations (*n*) on which the result is based.

Wire.	Diam. mm.	*n*.	$J/M \div (1{\cdot}13 \times 10^{-7})$.
Soft iron . . .	·36	21	·507
Hard iron . .	·28	2	·501
Soft iron . . .	·29	1	·500
Nickel . . .	·32	2	·505

TABLE XXII.—J/M FOR IRON AND NICKEL (CHATTOCK AND BATES).

The ratios found are, within the limits of experimental error, half those predicted theoretically, so that a striking "gyromagnetic anomaly" appears. Special investigations of Chattock and Bates showed that this could not be attributed to any kind of "slip" or lag in the reaction of the rod as a whole to the turning of the elementary magnetic orbits; for no after-effects could be detected in a period of several minutes.

3. Other Experiments

An early attempt to detect a gyromagnetic effect was made by Maxwell (1861). Assuming that magnetism was due to amperian molecular currents possessing inertia, Maxwell concluded that a magnetized rod should possess the properties of a gyroscope and that, if rotated about any axis, it should tend to set itself with its magnetic axis parallel to the axis of rotation. Using a cylindrical coil of wire in which an iron core could be inserted, a change in the equilibrium angle between its axis and the axis of rotation with reversal of the current or direction of rotation was looked for. No change could be detected, as indeed would be expected, even under the most favourable circumstances, on the basis of the present theories. In the later experiments it is effects which are due to change in orientation of the elementary electronic orbit magnets which are investigated. It is interesting that in 1890 Perry tried unsuccessfully to detect a change in magnetization of an iron rod by rotating it about its axis.

The results obtained in recent work will be stated by expressing the ratios found for J/M or H/ω as a fraction r of the theoretical value $\frac{2mc}{e}$ (1.1, 1.2, 2.4).

Richardson's experiments (1908) to detect the effect he had predicted led to no positive result, the method in essentials being that used later by Chattock and Bates. A modification in this first type of experiment was introduced by Einstein and de Haas (1915), a resonance method being employed to give increased sensitivity. The small iron rod was magnetized by an alternating field of variable frequency, which included the natural frequency of the suspended system. The amplitude of the oscillations induced was determined as a function of the frequency. From the maximum amplitude, maximum magnetic moment and the damping factor, it was possible to calculate J/M; and the sign could be determined from the phase relations. The first experiments yielded values in rough agreement with the theory. The same general method was again used by de Haas (1916), but the solenoid was wound directly on the iron rod under investigation, so that the torque on the rod and solenoid together was found. The results again seemed to accord with the theory, but very unfortunately only a few rough experiments were tried. The original Einstein and de Haas work was repeated with great improvements by Beck (1919) and extended to nickel. He found for iron $r = \cdot 53$ and for nickel $r \doteqdot \cdot 57$. Arvidsson (1919) also found for iron $r \doteqdot \cdot 5$. Stewart (1917) used the method which was subsequently improved by Chattock and Bates, examining the angular momentum produced by annulling the residual magnetism in small rods of iron and nickel. For both he found approximately $r = \cdot 5$. Sucksmith (1925) has found that $r \doteqdot \cdot 5$ for cobalt and magnetite.

The main investigator on the magnetization by rotation type of experiment has been S. J. Barnett. Started in 1909, the work was carried out in collaboration with L. J. H. Barnett, the first successful experiments in the whole field being made in 1914. The essential difficulties will be clear from the fact that theoretically (2.4), 3,000 revolutions per minute (giving $\omega = 2\pi \frac{3{,}000}{60}$) is equivalent to a field of only $3\cdot 55 \times 10^{-5}$ gauss. In all the methods the rod is mounted horizontally in a region where the earth's field is neutralized. The "intrinsic magnetic intensity of rotation" is determined by comparing the change of flux through the rod produced by rotation with that produced by the application of a field of known magnitude. The change in flux may be measured by a ballistic galvanometer of the fluxmeter type. Alternatively, the magnetic moment of the rotating rod may be measured by means of a galvanometer.

The first experiments carried out on cold rolled steel established the proportionality between H and ω, with the sign in agreement with the theory (clockwise rotation corresponding to north pole uppermost) and gave r about ·5. A more thorough investigation (1915) confirmed this. In 1917 steel, cobalt and nickel were examined, using a magnetometer method, and somewhat larger values for r were found, but since then (1922), "extensive and conclusive experiments" on these substances, and also on soft iron and Heusler alloy, have been carried out, all giving within the limits of experimental error $r = {\cdot}5$.

It may be concluded from the work of Chattock and Bates, and that which has been more rapidly reviewed, that for ferromagnetics generally the ratio between J and M, or between H and ω, although agreeing remarkably with theory as regards constancy and sign, has a value only half as great as that predicted.

4. Discussion of the Anomaly

The results of the gyromagnetic experiments are usually taken to indicate that the ratio of the magnetic to the mechanical moment of the elementary magnets in the substances investigated is actually twice that calculated on the basis of classical electron theory. The fact that the electrons move in quantum orbits does not affect the theoretical ratio—it merely restricts the possible magnetic and mechanical moments to certain definite discrete values. For a simple electronic orbit j is an integral multiple of $\frac{h}{2\pi}$, and μ of the unit magneton $\frac{eh}{4\pi mc}$. Although the resultant moments of an atom, or a "carrier," as a whole are not necessarily integral multiples of the unit, the ratio of j to μ will remain equal to $2mc$ to e.

In classifying the possible states of an atom as revealed by the multiplet structure and Zeeman-effect behaviour of the spectral lines, inner quantum numbers have been assigned to them (Ch. X). Though these are primarily chosen in such a way that certain selection rules for possible transitions are satisfied, there is good reason for supposing that they are related in some simple manner to the angular momentum of the atom as a whole, expressed in terms of the unit $h/2\pi$. Adopting Sommerfeld's classification, the inner quantum numbers (j') which he assigns have been supposed by him to give directly the angular momentum of the atom. Now the magnetic moment μ of an atom in any state may be deduced from Zeeman-effect observations, and the ratio of μ to j' found; this is given by the Landé splitting factor g—

$$\frac{\mu}{j'} = g \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

(μ and j' are measured in terms of the Bohr units). The Landé splitting factor may be calculated from a generalized, but essentially empirical, expression, for any of the atomic states. For atoms in an s state, with the series electron in a $k = 1$ orbit (but practically only for these), $g = 2$. Thus, if the carriers in ferromagnetics were atoms in an s state, the gyromagnetic result might be taken to uphold the view that j' actually gives a measure of the angular momentum of the atom, and would lend support to a treatment of the Zeeman effect based on this. While the gyromagnetic anomaly would then appear simply as a special case of a much more general series of anomalies, it would remain "unexplained"; and the acceptance of such an anomaly as fundamental, and virtually inexplicable, is absolutely unsatisfying to normal scientific intellectual desires. For the atoms of iron, nickel, and cobalt, the normal state is not an s state. For the carriers in the solids, however, nothing definite can be said, but, while it is unlikely that any of them are in an s state in the usual sense of the term, it is certainly highly improbable that the state of the carriers in all the substances whose gyromagnetic effect has been examined is the same, though the same anomalous ratio is found for all of them.

Richardson has pointed out that a ratio for j/μ for an atom differing from $2mc/e$ would be expected if the nucleus as well as the electrons moved in a quantum orbit. Let j_e, μ_e be the electronic moments, j_n, μ_n the nuclear; suppose j_e and j_n are oppositely directed; and let E, M be the nuclear charge and mass. Then—

$$j = j_e - j_n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.1)$$

$$\mu = \frac{e}{2mc} j_e + \frac{E}{2Mc} j_n \quad . \quad . \quad . \quad . \quad . \quad (7.2)$$

Since $\frac{E}{M}$ will be of the order of $10^{-3}\frac{e}{m}$, approximately

$$\frac{j}{\mu} = \frac{j_e - j_n}{j_e}\left(\frac{2mc}{e}\right) \quad . \quad . \quad . \quad . \quad . \quad (7.3)$$

—accounting for the results if, for example, $j_e = 2$, $j_n = 1$, in terms of the Bohr unit. Though this idea is ingenious, and can fluxmeter type. Alternatively, the magnetic moment of the rotating rod may be measured by means of a galvanometer.

The first experiments carried out on cold rolled steel established the proportionality between H and ω, with the sign in agreement with the theory (clockwise rotation corresponding to north pole uppermost) and gave r about ·5. A more thorough investigation (1915) confirmed this. In 1917 steel, cobalt and nickel were examined, using a magnetometer method, and somewhat larger values for r were found, but since then (1922), "extensive and conclusive experiments" on these substances, and also on soft iron and Heusler alloy, have been carried out, all giving within the limits of experimental error $r = {\cdot}5$.

It may be concluded from the work of Chattock and Bates, and that which has been more rapidly reviewed, that for ferromagnetics generally the ratio between J and M, or between H and ω, although agreeing remarkably with theory as regards constancy and sign, has a value only half as great as that predicted.

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—accounting for the results if, for example, $j_e = 2$, $j_n = 1$, in terms of the Bohr unit. Though this idea is ingenious, and can result arrived at is unfortunately elusive, but the calculation is given for what it is worth.

The energy of a system of elementary magnets (cf. II, 32.2) is given by

$$W = -\Sigma\tfrac{1}{2}\mu H$$

so that $-\frac{1}{2}\mu H$ may be regarded as the intrinsic energy of a single elementary magnet in a field. Let i be the moment of inertia of the electrons in a carrier. Then, for a diamagnetic carrier, when a field is brought into existence, the change in kinetic energy—the only change—$\triangle T$, is given by

$$\triangle T = \tfrac{1}{2}io^2.$$

The magnetic moment acquired being μ, and j $(= io)$ the mechanical moment, equating the two energy expressions—

$$\tfrac{1}{2}jo = -\tfrac{1}{2}\mu H \quad \text{. . . . . . .} \quad (9)$$

giving, as before

$$\frac{j}{\mu} = -\frac{H}{o} = \frac{2mc}{e} \quad \text{. . . . . .} \quad (9{\cdot}1)$$

A paramagnetic carrier has an initial moment j_0 and angular velocity ω_0 $\left(j_0 = i\omega_0 \text{ and } j_0 = \frac{2mc}{e}\mu\right)$. A similar calculation to the above gives

$$\triangle T = \tfrac{1}{2}i(\omega^2 - \omega_0^2) = \tfrac{1}{2}i[(\omega_0 + o)^2 - \omega_0^2] = -\tfrac{1}{2}\mu H$$

$$\tfrac{1}{2}i\omega_0\left[2o + \frac{o}{\omega_0}\right] = -\tfrac{1}{2}\mu H$$

$$\frac{j}{\mu} = -\frac{H}{o} = \frac{mc}{e} \quad \text{. . . . . .} \quad (9{\cdot}2)$$

as long as o/ω_0 is small.

This seems to suggest that whereas for a diamagnetic carrier the whole of the reaction corresponding to its acquisition of a moment is exerted against the field, for a paramagnetic carrier, half is. The total momentum of a carrier is j_0, but only half (instead of the whole) of this will appear as reaction momentum in the rod as a whole. This is exactly what is observed. The calculation is not, however, regarded as giving an explanation, but it does seem to indicate that comparatively normal roads for the explanation of the anomaly are not yet closed.

Even if the imposition on an actual carrier of an angular velocity ω is precisely similar in its effects to the application of a field H of magnitude $-\frac{2mc}{e}\omega$, its imposition on a solid rod would not be expected to have the same magnetic effects, owing to the peculiar nature of the interaction between the carriers and the rest of the structure revealed by the results of the Richardson type of experiment. The Barnett type of experiment will yield the same value for the gyromagnetic ratio, provided that the alternative expressions (2.2) and (2.3) for the torques are really equivalent. The two types of experiment, though not simply converse, are reciprocal; the results of both will have the same basic explanation.

In the latter part of this discussion it has been assumed that the ratio of j to μ for the elementary carriers is the theoretical one; and it has been suggested that an explanation of the experimental anomaly may be found if the reaction to the orientation of a paramagnetic electron orbit is not wholly taken up by the system as a whole of which it is part, but also by the system giving rise to the magnetic field. The suggestion is tentative, and may be wholly wrong; the problem is a difficult one. All possibilities, however, should be explored before essentially fundamental theory is abandoned.

Experimentally, the need for investigation of diamagnetics can hardly be over emphasized; and valuable results might be obtained from a careful repetition of experiments of the de Haas type, in which is measured the total reactional angular momentum on the rod and the magnetizing system.

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This is the basis of section 3.

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CHAPTER IX

THE MAGNETIC DEVIATION OF ATOMIC RAYS

1. Theory of the Experiments

THE theory of spatial quantization was put forward independently by Sommerfeld and Debye in 1916 as a necessary basis for the quantum treatment of the Zeeman effect. It led to the conclusion that the resolved magnetic moment of an atom in the direction of an applied magnetic field, could only assume certain discrete values—a conclusion at first sight very surprising, but one which received indirect experimental support in so far as it enabled Zeeman effect phenomena to be satisfactorily correlated. In the Zeeman effect, however, it is the difference in the energy in the atom in two different states which is actually determined; while ordinary magnetic measurements give only the mean effect of a large number of differently orientated atoms. Fortunately, the theoretical conclusions may be experimentally tested in a very direct manner, by examining the deviation of a stream of atoms in a non-homogeneous magnetic field. In the investigations carried out by Gerlach and Stern, at Frankfurt (1921 onwards), possible magnetic moments of atoms in the field direction are determined; the beauty of the experiments themselves, and the theoretical significance of the results, combine to make the research one of outstanding interest and fundamental importance.

In the experiments the element under investigation is heated in a small oven, and the evaporating atoms escape through an aperture; by means of a suitable system of slits a narrow, unidirectional stream of atoms is produced, the velocity of the atoms depending on the oven temperature. The stream passes through a region in which a non-homogeneous field may be applied, the field and its gradient being at right angles to the stream, and the atoms impinge on a glass plate, forming a thin deposit, which can be rendered visible; from the traces obtained (giving the cross-section of the stream) with and without the field the deviation produced by the field may be determined.

Let μ be the magnetic moment of the atom in the field direction, s the direction of the field gradient, F the force on the atom. Then (cf. II, 18, etc.)

$$F = \mu \frac{\partial H}{\partial s} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(F, μ, H and s being unidirectional, it is unnecessary to employ vector notation). Suppose that in the absence of a field the stream has a small circular cross-section, so that the trace is a small circle, and consider the form of the trace which would be anticipated when the experiment is carried out with the field applied—first on the quantum theory (taking a simple case, for which the theory predicts $\mu = \pm \mu_1$), and then on the classical theory. The forms of the traces are represented in Fig. 35.

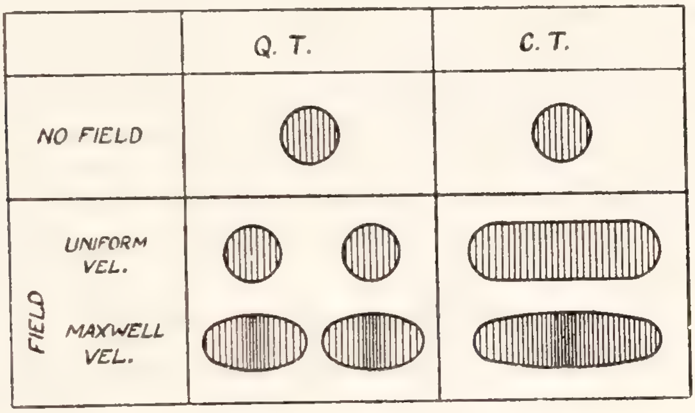

FIG. 35.—Anticipated Forms of Traces.

On the quantum theory, a uniform velocity stream would give rise to two similar traces, equally displaced from the zero position; if, however, the velocity distribution is Maxwellian, the traces will be elongated, and will have regions of maximum density corresponding to the most probable velocity. The zero position will be marked by a pronounced minimum. On the classical theory, any orientation of the magnetic electron orbit is equally probable; let a be the angle between H and the magnetic axis; then (1) becomes

$$F = \mu_1 \frac{\partial H}{\partial s} \cos a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Let s be the displacement on the plate of the portion of the trace corresponding to a definite set of atoms, whose magnetic axes lie within an angular range da. For uniform velocity, with $k_1 \ldots k_4$ constants,

$$s = k_1\mathrm{F}. \qquad \mathrm{F} = k_2 \cos a. \qquad dn = k_3 \sin a da.$$

$$\frac{ds}{da} = k_1 k_2 \sin a$$

$$\frac{dn}{ds} = \frac{k_3}{k_1 k_2} = k_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.1)$$

A trace extending from $s = k_1\mu\frac{\partial \mathrm{H}}{\partial s}$ to $s = -k_1\mu\frac{\partial \mathrm{H}}{\partial s}$ will be produced, of uniform density. For Maxwellian velocity distribution the trace will be more elongated, but the deposit at the edges will be produced only by the atoms of low velocity, while atoms of any velocity (owing to the different orientations) may affect the centre of the trace. Thus the quantum theory predicts, for Maxwellian velocity distribution, an intensity minimum in the zero position, the classical theory an intensity maximum. A sharp distinction between the two theories will be possible, provided the experimental technique can be sufficiently refined that the displacements are appreciably greater than the breadth of the zero trace. Some of the experimental details will now be briefly considered.

2. Apparatus and Procedure.

The apparatus is represented very diagrammatically in Fig. 36.

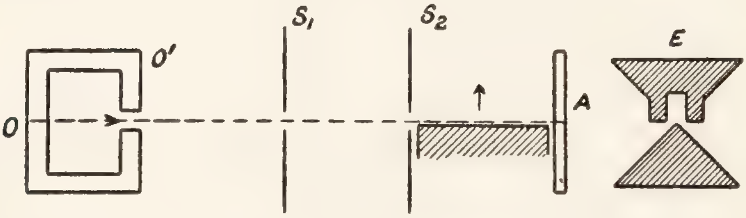

FIG. 36.—Diagram of Gerlach and Stern Apparatus.

The stream of atoms issuing from the aperture O′ in the electric oven O is delimited by the slits S_1 and S_2, and then passes through the field region to be received on the plate A. The non-homogeneous field is produced by an electromagnet with pole pieces of the wedge groove type, shown in section at E. One of the main experimental difficulties lies in the adjustment and maintenance of the constituent parts of the apparatus in such positions that a straight atom stream path OA is obtained ;

owing to the necessarily small dimensions of the slits, this adjustment must be very exact. In the later experiments, matters were so arranged that the " line " OA was undisturbed by evacuating processes, and that the slits could be widened and cleaned without necessitating readjustments. The construction of the oven presents difficulties, for it must be capable of withstanding a high temperature, and this must be under delicate control as regards constancy over long periods. Another problem arises in the development of the traces to render them visible ; for many of the elements, the plate must be cooled with liquid air in order to obtain the initial deposit.

Magnet wedge pole pieces 30 mm. long (angle 90°) and 47 mm. long (angle 60°) were used ; the slits were fixed to an extension of brass. The slit pieces ($2\frac{1}{2} \times 3\frac{1}{2}$ mm.) each comprised two slits, one limiting the breadth, the other the length of the cross-section of the beam. The magnet wedge was placed in a dovetailed brass piece B (Fig. 37), so that it could be firmly

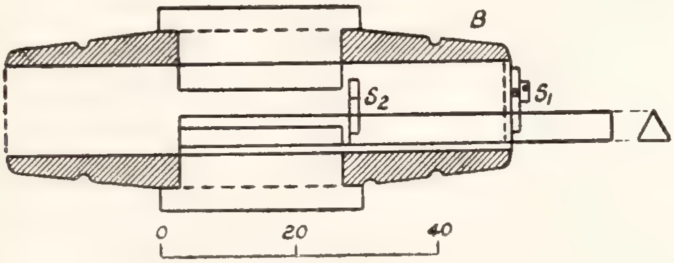

FIG. 37.—Pole-piece Section of Apparatus.

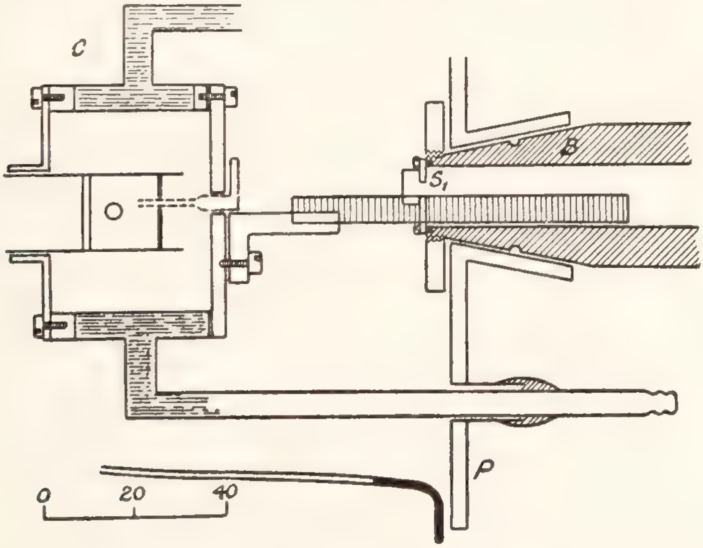

FIG. 38.—Details of Apparatus.

attached to the brass plate P (Fig. 38). (Note that Fig. 37 is reversed as compared with Figs. 36, 38 and 39.)

The oven with its surrounding cooler was all enclosed in a glass tube of bell-jar form (Fig. 39), a ground-glass grease joint to P proving satisfactory. Grooved pole pieces of various sizes and heights were employed. These could be firmly fixed above the wedge pieces.

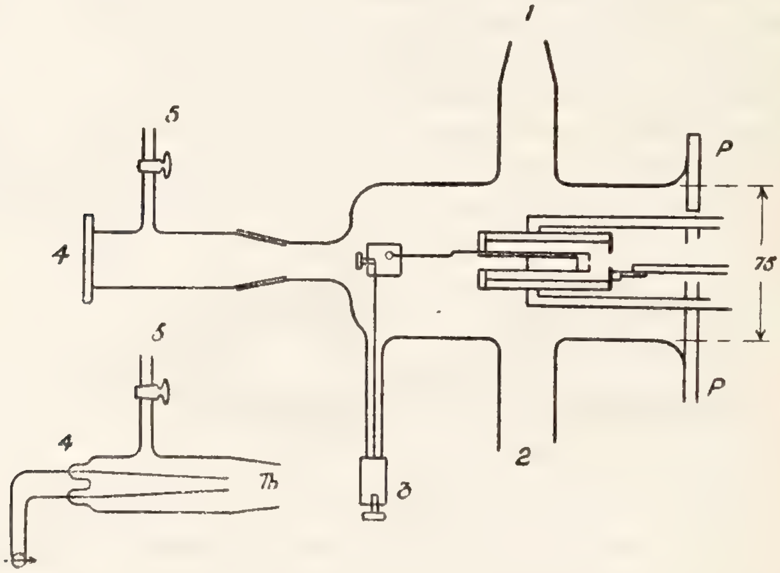

Fig. 39.—Oven End of Apparatus.

1. To pump.
2. To charcoal-liquid air.
3. Oven-heater leads.
4. Thermoelement, or plate.
5. Inlet for dry air, or nitrogen.

The oven itself, cylindrical in form (some 20 mm. × 7 mm.) had a 1·2 mm. aperture; the oven-cooling cover C (about 30 mm. diam.) had a slightly larger opening. In the early work, a small iron oven was used; but later a larger porcelain oven was substituted, to increase the range of temperatures available—so increasing the density of the atomic stream, and decreasing the time required to produce traces, and enabling more elements to be studied. A maximum temperature of about 1,700° could be attained with a heating current of 2·5 amp. and 200 watts. The temperature was determined thermoelectrically below 1,000° and optically above (see Fig. 39).

The methods for vacuum control were the usual, the oven-cooler section (O—S_1 in Fig. 36) and the remainder of the apparatus being evacuated separately.

The slits S_1 S_2 and the oven and cooler apertures were aligned, using a telescope. The slit pieces had their plane sides towards the oven, and to S_1 a larger plate was attached so that the progress of deposition could be observed. The pole pieces (that is, the whole section shown in Fig. 37) were clamped between the poles of a firmly mounted du Bois electromagnet, and the entire apparatus formed a rigid whole. In some of the experiments cross-fibres of quartz were mounted on the plate end of the wedge pole piece, so as to give a reference " shadow " mark on the plate.

The traces obtained on the glass plate (about 3 mm. square), which must be scrupulously clean, were " developed " (physically) by being placed in 60 c.c. of a 1 per cent. hydroquinone solution to which was added 1 c.c. of 1 per cent. silver nitrate solution and a trace of gum arabic. The process worked well for Ag, Au, Cu, Sn, and Ni. With Bi, Sb, Fe, Pb and Tl it was increasingly difficult to obtain satisfactory traces. With elements requiring high temperatures the deposition of grease and mercury on the plate caused much trouble, while with Fe the thin deposits of the element tend to oxidize rapidly unless great precautions are taken. The process of development had to be controlled by taking microphotographs at intervals, partly to test whether any change in the form of the trace occurred, and partly because over-development may obscure some of the features.

In carrying out an experiment, a long evacuation is first necessary, liquid air and charcoal being employed. The oven temperature, the vacuum and the magnetic field current then have to be kept constant for the period of the experiment. At first 4–10 hours was required, but this was reduced, with the apparatus described, to about 45 minutes. Preliminary experiments were made to find the time and temperature necessary; and the oven had to be heated up for a considerable time before constancy of temperature could be maintained. Finally the plate, frequently with no initial trace visible, had to be developed in stages. It is not surprising that of many experiments begun, few were carried to a successful conclusion.

The inhomogeneity of the field $\frac{\partial H}{\partial s}$ was determined from separate measurements of H and $H\frac{\partial H}{\partial s}$. The field was found from the change of resistance of a bismuth wire. To find $H\frac{\partial H}{\partial s}$ a small bismuth wire (3 mm. long, $\frac{1}{10}$ mm. diam.) was suspended in the field by a delicate frame of quartz so supported that the couple due to the force on the bismuth wire (depending on

$\kappa H\frac{\partial H}{\partial s}\Big)$ could be counterbalanced by that produced by placing riders on a transverse arm of the frame. A mirror was attached to the frame. On the application of the field the frame could be accurately brought back to the zero position. The following numbers give an idea of typical values of H and $\frac{\partial H}{\partial s}$ at a distance *d* from the edge of the wedge pole piece:

d mm.	H Gauss.	$\partial H/\partial s$ Gauss cm.$^{-1}$.
·15	$17{\cdot}5 \times 10^3$	236×10^3
·60	$12{\cdot}8 \times 10^3$	76×10^3

Control experiments were always performed without the application of a field. Silver was first investigated very completely, many series of experiments being made; with other elements, it was then possible to test whether the apparatus was working properly by interpolating experiments with silver.

3. Results

In the first experiments with silver the "slit system" consisted of a capillary tube of $\frac{1}{20}$ mm. bore, and the effect of the field was simply to widen the circular trace into an ellipse with diffuse edges. The broadening, however, was small, and no conclusions could be drawn. A slit system similar to that finally employed was substituted. In the absence of a field a sharp line was obtained. With a field, the line definitely divided into two, and there was a marked intensity minimum in the undisplaced position. The quantum theory had triumphed! Experiment had verified that in a magnetic field, the resolved moment of the silver atom assumed two discrete values; but this was only a first step. The refining of the apparatus so that precise and more extended measurements might be made still required great skill and patience. Some of the results obtained with the apparatus which has been described will now be considered.

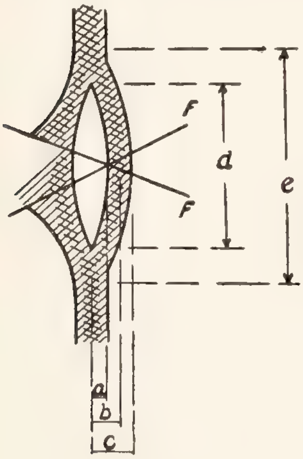

Fig. 40.

Absolute Determination of the Bohr Magneton.—The general form of the trace obtained with silver is represented, much magnified, in Fig. 40.

The left-hand component, corresponding to the attracted beam, is diffuse on one side owing to the strong and varying inhomogeneity of the field near the wedge pole piece towards which the atoms are deflected. The mean deviation of the repelled beam $\left(b \doteq \frac{a+c}{2}\right)$ can, however, be measured with fair accuracy. Let v be the velocity of the atom stream. According to theory, using m for the atomic mass,

$$\tfrac{1}{2}mv^2 = \frac{3}{2}kT$$

giving
$$v = \sqrt{3}\sqrt{\frac{kT}{m}} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Some previous experiments, in which the deflection of the atoms under the influence of a gravitational field had been investigated, had shown that the factor for the mean velocity was more closely $\sqrt{4}$. A mean of the two values was assumed—

$$v = \sqrt{\frac{3{\cdot}5kT}{m}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3{\cdot}1)$$

For the displacement s, due to the stream passing through a length l (S_2A in Fig. 36—the length of the wedge pole piece) in which the inhomogeneity is $\left(\frac{\partial H}{\partial s}\right)_0$

$$s = \frac{1}{2}\frac{F}{m}\left(\frac{l}{v}\right)^2$$

$$= \frac{1}{2}\mu\left(\frac{\partial H}{\partial s}\right)_0 \frac{l^2}{3{\cdot}5kT}$$

$$\mu^{-1} = \frac{1}{2}\cdot\frac{1}{s}\cdot\left(\frac{\partial H}{\partial s}\right)_0 \frac{l^2}{3{\cdot}5kT} \quad . \quad . \quad . \quad . \quad . \quad (3{\cdot}2)$$

or, for the gram-atomic moment M,

$$M^{-1} = \frac{1}{2}\cdot\frac{1}{s}\cdot\left(\frac{\partial H}{\partial s}\right)_0 \frac{l^2}{3{\cdot}5RT} \quad . \quad . \quad . \quad . \quad . \quad (3{\cdot}3)$$

A correction has to be applied to this for the variability of the inhomogeneity owing to the curvature of the beam, which is nearer the pole piece at S_2 than at A. If $\left(\frac{\partial H}{\partial s}\right)_0$ and $\left(\frac{\partial H}{\partial s}\right)_l$ are the corresponding gradients, the full expression, due to Stern, is

$$M^{-1} = \frac{1}{2}\cdot\frac{1}{s}\cdot\left(\frac{\partial H}{\partial s}\right)_0 \frac{l^2}{3\cdot5RT}\left[1 + \frac{1}{12}\,\frac{\left(\frac{\partial H}{\partial s}\right)_l - \left(\frac{\partial H}{\partial s}\right)_0}{s}\,\frac{Ml^2}{3\cdot5RT}\right] \quad (3\cdot4)$$

In a typical experiment with silver, the slits were at a distance of ·32 mm. from the wedge pole-piece edge; their apertures— S_1, ·10 × ·2 mm.; S_2, ·063 × 1·2 mm.; $\left(\frac{\partial H}{\partial s}\right)_0 = 13\cdot4 \times 10^4$; $\left(\frac{\partial H}{\partial s}\right)_l = 8 \times 10^4$ gauss cm.$^{-1}$; temperature 1,020° ± 10; mean deviation of repelled beam ·21 ± ·01 mm. These data lead to a value of the gram-atom magneton of 5,690, which differs by only 2 per cent. from the theoretical value of 5,593 (V, 23.2). In some previous experiments deflections of ·10 and ·15 mm. were observed, corresponding to calculated values of ·101 and ·146 mm. The experimental magnetic moment of the silver atom is equal, within the limits of error, to one Bohr magneton.

Experiments were carried out with Cu and Ag under the same conditions as to distances and field; the temperature for Cu was 1,700°, for Ag 1,400°.

$T_{Cu}/T_{Ag} = 1\cdot2$. For s_{Ag}/s_{Cu} the ratios 1·2 and 1·3 were found. Since $s \propto \frac{1}{T}$ (3.2), the magneton value found is confirmed with a second element.

Atomic Magnetic Moments.—Copper (29), silver (47), and gold (79) all gave traces corresponding to moments, expressed in terms of the Bohr unit, of $\mu = \pm 1$.

With thallium (81) the trace divided into two, there being a definite absence of undeviated atoms; but the separation was small, corresponding approximately to $\mu = \pm \frac{1}{3}$.

No effect of the field was found for tin (50) and lead (82), a number of experiments being tried with both. $\mu = 0$.

The same applies to zinc (30), cadmium (48), and mercury (80). $\mu = 0$.

With antimony (51) and bismuth (83) there is probably a considerable proportion of molecules in the stream. Sb showed only the undeviated trace; the Bi trace was remarkable in showing a one-sided continuous broadening, indicating not only undeviated, but also strongly attracted carriers.

The nickel (28) trace, represented diagrammatically in Fig. 41, showed a very complex structure. There were three sharply marked maxima, including one in the undeviated position. The distance between these was greater than that between the undisplaced position and the deflected trace for silver (·18 compared with ·12 mm.) for the same fields, although the temperature was higher (1,400°–1,500°); values are indicated for μ of -2, 0 and $+2$. In addition to the three pronounced maxima, there are definite indications of the presence of atoms of moment considerably greater than 2.

In dealing with iron (26) very high temperatures had to be employed. The initial deposit was almost invisible. On development a fine line of uniform intensity appeared at first, but attempts at intensifying produced unsatisfactory "flecks." All that can be said is that the application of the field led to no intensity decrease, or widening, indicating that for Fe $\mu = 0$.

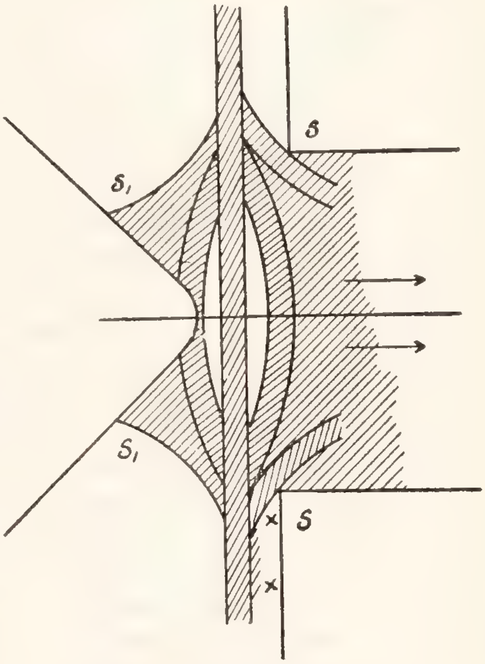

FIG. 41.—Nickel Trace.

4. Discussion of Results

The magnetic deviation experiments give directly the resolved moments of the carriers, and it is necessary to consider whether these consist of single atoms. At the temperatures employed, there is little doubt that the vapours of Cu, Ag, Au, Sn, Pb, and Tl are monatomic, so that the μ's deduced do correspond to atomic moments. For Pb carriers of very small moment would have been detected owing to the low temperature; for Sn $\mu = \pm \frac{1}{2}$ would have produced appreciable widening, but not $\mu = \pm \frac{1}{3}$.

The molecular weight of bismuth (atomic weight 208) at 1,650° is 350; some atoms are present, but there is a large proportion of molecules, and the remarkable one-sided widening is probably to be attributed to molecular magnetic peculiarities. Antimony (atomic weight 120) has a molecular weight of 284 at 1,640°, so very few atoms are present. This agrees with the fact that the absorption spectrum of the vapour is of the molecular type (Grotrian). Nickel and iron are probably monatomic.

The discussion of the results obtained for the atomic moments will be more conveniently taken up when atomic magnetic properties are considered in relation to the periodic system as a whole (Ch. XIV) after the Zeeman effect has been dealt with (Ch. X); but the main points emerging may be briefly indicated here with reference to the quantum theory of atomic structure already outlined (Ch. V, sect. 2). In accordance with the scheme put forward, atoms with a "closed configuration" should be diamagnetic, having no resultant magnetic moment. In their normal state Cu, Ag and Au atoms have one electron moving in an *s* orbit ($k = 1$) external to a "completed" core; due to this electron, the atom should possess unit magnetic moment. The setting of the electron orbit at right angles to the field (Ch. V, sect. 5) gives rise to atoms with resolved moments of $+ 1$ and $- 1$ (in terms of the Bohr unit). The experimental results are completely and naturally in agreement with theory. Zn, Cd and Hg have two electrons added to a closed configuration. Their normal state, as indicated by the spectra, is the singlet S state, in which, as the Zeeman effect shows, the magnetic moment is zero—which, again, is quite naturally accounted for by supposing that the two electrons move in opposite directions in orbits (not necessarily exactly equivalent) corresponding to the same azimuthal quantum number. In Sn and Pb the four outer electrons form a partially complete configuration (the OI, II, and the PI, II levels being filled up respectively), and the magnetic moment is zero. Thallium (81) has three added electrons, and it is not possible to predict what its moment will be from simple upbuilding considerations. The absorption spectra, however, show that the normal state is a p_1 state corresponding to a doublet series; the Zeeman effect indicates an *mg* value (which corresponds to μ in the sense in which it has been used in this chapter) for a p_1 state of $\pm \frac{1}{3}$, which agrees with the Gerlach and Stern result.

Nickel is the first element for which the deviation experiments have revealed directly the numerically different resolved moments which an atom may have, corresponding to the different magnetic term components in the Zeeman effect. The Ni spectrum shows singlets, triplets and quintets. Possible resolved moments anticipated from the Zeeman effect for the atom in an *s* state would then be $0, \pm 2, \pm 4$. This is suggestive, but as the normal spectroscopic state corresponds to a triplet *f* term, no conclusions can yet be drawn. The iron spectrum consists of odd multiplets, and a zero moment is possible; other moments would, however, also be expected from the spectra, for the series electron is most firmly bound in *d* quintet level, for which moments ranging from 0 to 6 would be anticipated; this is a real difficulty which remains to be cleared up. The reason for the "anticipations" for Fe and Ni will be clearer from the next chapter. It may be worth noting, however, that undeviated traces may be quite generally anticipated for atoms which give rise to spectral series of odd multiplicity; but for atoms giving even series, there should be no undisplaced trace.

In the silver experiments no difference could be detected in the intensity of the two displaced traces, which appeared simultaneously on development. If the relative number of atoms with magnetic axes in the same (n_1) direction as the field, and in the opposite (n_2), follow a Boltzmann law

$$n_1 : n_2 = e^{\frac{\mu H}{kT}} : e^{-\frac{\mu H}{kT}} = e^{\frac{2MH}{RT}} : 1 \quad . \quad . \quad . \quad . \quad (4)$$

Taking $M = 5{,}593$, $H = 2 \times 10^4$, $T = 1{,}300$, this gives

$$n_1 : n_2 = 1{\cdot}0021 : 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.1)$$

Very much larger fields would be required to produce an appreciable difference in the traces.

It might seem that the "opposed" atoms would be unstable, but it must be remembered that the dynamical equilibrium conditions differ greatly from those for a gross magnet in a field. Calculations show that for a hydrogen atom with the plane of the electronic orbit at right angles to the field, an arbitrary disturbance produces only periodic, not aperiodic, changes in the undisturbed orbit, in whichever direction the electron rotates. The stability is intelligible if a field simply has the effect of changing the angular velocity of the electron.

The great problem as to the mechanism of orientation comes prominently to the fore in these experiments. It has been discussed in this connection in particular by Einstein and Ehrenfest (1923). The atoms, presumably orientated at random in the field-free oven region (which was magnetically shielded). are shown by the experiments to have assumed discrete orientations in the field. As has been emphasized, the direct effect of a field is simply to give rise to precession without orientation. In the unidirectional stream there cannot be interatomic collisions. Nevertheless, some of the atoms (those whose axes finally point in the field direction) lose energy, others gain energy. There seems no other possible mechanism than the emission and absorption of radiation, energy being lost to or gained from the field. As may readily be calculated from the velocity of the atoms, and the apparatus dimensions, the orientation must occur in a period of the order of 10^{-4} seconds. This is very long compared with the period of revolution of the valence electron (of the order of 10^{-15} seconds), so that the process may be regarded as relatively slow (of the "adiabatic transformation" type). On the other hand, if the orientation were due to the emission and absorption of the temperature equilibrium radiation, a period of 10^9–10^{11} seconds would be required. If this is assumed to be the mechanism, it is necessary to suppose that the "reaction velocity" is enormously greater for transitions of the atom between a non-quantum and a quantum state, than between two quantum states. Though this supposition might be true, the general "explanation" which it would suggest seems unconvincing. The alternative is to suppose that, at least during "slow" transformations, the atom is continuously maintained in a quantum state. (The difficulties arising in connection with very small fields, and whose experimental investigation promises to shed much light on quantum dynamics generally—see Ch. XI—do not enter prominently here.) The atom assumes a quantum orientation relative to the resultant field, which can never change "abruptly." The view is in harmony with the spirit of the quantum theory. Difficulties are not explained, but they are brought into relation with the fundamental problem as to why there are certain differentiated "quantum states" which are stable while others are not. It is still necessary to suppose that the atoms, in the magnetic deviation experiments, as they pass from the relatively field-free region into the field, are maintained in a quantum state by gain or loss of energy by radiation. It would seem that this must be virtually continuous and of indefinitely long wavelength! It might here be noted, as a point of general application, that while it is frequently convenient to regard atoms as quantized systems in a field, the field itself arises from a mechanism composed of parts to which quantum rules apply; so that the atoms on which attention is primarily directed simply form a part of a larger system which as a whole is subject to quantum dynamical laws, and which assumes a quantum state compatible with them.

It may be tentatively concluded that in the Gerlach and Stern experiments the atoms, or the electronic orbits, although there are no interatomic collisions, assume quantum orientations in the field, the energy changes involved being brought about by a quasi-radiational mechanism. For weak fields the numbers of atoms in the different possible states will be equal. It should be noted that whether the conditions would allow of the abrupt changes of orientation, which the attainment of a temperature equilibrium distribution (4) would require, is a further distinct question, irrevelant in connection with the magnetic deviation experiments, though of vital importance in connection with paramagnetism generally (see Ch. XVI, sect. 2).

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CHAPTER X

THE ZEEMAN EFFECT

1. Introductory

THE influence of a magnetic field on spectral lines was first observed by Zeeman in 1896, as has been mentioned in Chapter I. The importance of the phenomenon for spectral and atomic theory was at once recognized, and since then, particularly under the inspiration of the quantum theory, an enormous amount of experimental and theoretical work has been carried out, of which only the slightest sketch can be given here, with little reference to the many individual investigators through whose labours the present outlook has been reached. The simplest effect is shown by lines of singlet series. Observed transversely to the field, these lines split up into a "normal" triplet; the central undisplaced component is plane-polarized with the electric vector parallel to the field ($\parallel$ or π component), and the outer components, equally displaced, are plane-polarized with the electric vector at right angles to the field ($\perp$ or σ components). Longitudinally, two components are observed, displaced equally and oppositely from the zero position, and circularly polarized in opposite directions. A theoretical explanation of this splitting was given by Lorentz (1900) on the basis of the classical electron theory, which, although now superseded, was of great value and has much historical interest. The argument may be simply outlined. Consider an electron vibrating in an atom. Its motion may be resolved along and at right angles to the field. The parallel vibrations, uninfluenced by the field, produce no longitudinal effect (cf. II, 53 and 54) and an undisplaced $\parallel$ component transversely. The perpendicular vibrations may be regarded as compounded of two opposite circular vibrations, of frequency ν. The effect of the magnetic field on the motion of the electrons is to superimpose an angular velocity o $\left(=\dfrac{eH}{2mc} \text{ from IV, 8}\right)$; so that the change in frequency will be given by

$$\triangle\nu = \pm \frac{o}{2\pi} = \pm \frac{eH}{4\pi mc} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Observing in the direction of the field, electrons vibrating in a clockwise direction will have their frequency increased. The polarization observed longitudinally is in agreement with this. Transversely, the polarization will be linear (⊥). From (1) $\frac{e}{m}$ may be calculated from observations on normal triplets. Alternatively, putting in the value of $\frac{e}{mc}$ ($1 \cdot 77 \times 10^7$), and writing $\triangle\nu_n$ for the "normal" separation—

$$\triangle\nu_n = \frac{c\triangle\lambda_n}{\lambda^2} = 4 \cdot 70 \times 10^{-5}\, cH \quad . \quad . \quad . \quad (1.1)$$

According to Paschen and Back, nine helium lines give for $10^5\triangle\nu/Hc$ values ranging from 4·64 to 4·74; singlet lines of Cd, Zn, Hg, Mg, Ca also give normal separations.

The classical theory was unable to account for the more complicated types of line splitting. Independently of this, the mere existence of sharp spectral lines constitutes a fundamental difficulty (Ch. II, sect. 6, and Ch. V).

On the quantum theory the frequency of the electron in the atom bears no direct relation to that of the radiation emitted, which depends on the difference in energy of the atom in the states preceding and following an emission transition. According to the second fundamental postulate (V, 11)—

$$\nu = \frac{1}{h}(E_1 - E_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Any changes in the frequency of a line due to an imposed field must be sought in the changes in the energy of the atom in its initial and final states. Let $\triangle E$ be the change in energy corresponding to a stationary state due to a field H. Let m be the equatorial or magnetic quantum number, defining the resolved angular momentum of the electron in the field direction (m_0 will be written for the electronic mass). Then, assuming spatial orientation to occur, following the reasoning of Chapter V (Equations 30, etc.)

$$\triangle E = \triangle(\tfrac{1}{2}m_0 r'^2 \omega'^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The field gives rise to a precession, with angular velocity o, so that for the resolved angular velocity

$$\triangle\omega' = \omega' - \omega_0' = o \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.1)$$

and since there is no change in the form of the orbit, so that the total change in energy is equal simply to the change in kinetic energy,

$$\triangle \mathrm{E} = \tfrac{1}{2}m_0 r'^2\{(\omega_0' + o)^2 - \omega_0'^2\}$$

$$\fallingdotseq (m_0 r'^2 \omega_0)o \tag{3.2}$$

neglecting second-order terms in o.

Since

$$m_0 r'^2 \omega_0' = m\frac{h}{2\pi} \tag{3.3}$$

$$\triangle \mathrm{E} = mh\frac{o}{2\pi} \tag{3.4}$$

For the equivalent frequency change (cf. (2))—

$$\triangle \nu = m\frac{o}{2\pi} = m\triangle \nu_n \tag{3.5}$$

(3.5) gives the frequency change for the term. Let m_1 and m_2 be the magnetic quantum numbers for the initial and end states. Then, for the line, from (2)—

$$\triangle \nu = (m_1 - m_2)\triangle \nu_n \tag{3.6}$$

If m_1 and m_2 can assume any integral values, the quantum theory would suggest the possibility of components at multiples of the normal interval. These have been observed in strong fields. Ordinarily, however, a "selection principle" must be introduced, according to which

$$\triangle m = \pm 1 \text{ or } 0 \tag{3.7}$$

This implies a restriction in the possible changes in the resolved angular momentum, and though the ultimate significance may be obscure—it is connected with the angular momentum which may be associated with the radiation itself—the principle derives justification both from experiment and the correspondence principle. Classically, the angular momentum M associated with a circularly polarized wave system (that emitted by a circularly rotating electron) is related to the energy E by the equation

$$\frac{\mathrm{M}}{\mathrm{E}} = \frac{1}{2\pi\nu} \tag{4}$$

so that, for the change in momentum of the radiating system

$$\triangle \mathrm{M} = \triangle \mathrm{E}/2\pi\nu \tag{4.1}$$

This suggests that, on the quantum theory, since $\triangle E = h\nu$, a change of M of $\frac{h}{2\pi}$ (or a change in m of unity) will result in circularly polarized radiation. On the other hand, radiation arising from a linearly vibrating electron, classically, has no associated angular momentum—suggesting that $\triangle m = 0$ corresponds to linear polarization. These considerations give some theoretical support for the experimentally justified restriction of (3.7). The result of the simple quantum-theory treatment is, then, given by (3.6) and (3.7); to these should be added—

$$\triangle m = \pm 1 \rightarrow \text{Circular Polarization} \quad . \quad . \quad (5.1)$$
$$\triangle m = 0 \quad \rightarrow \text{Plane Polarization} \quad . \quad . \quad . \quad (5.2)$$

—$\triangle m = \pm 1$ giving rise to the ⊥ components, $\triangle m = 0$ to the ∥ components, in the transverse effect.

If the assumption is made that the m's in (3.6) must be integral (that is, that the resolved angular momenta of the atoms as wholes in the field direction must be integral multiples of $h/2\pi$), it is clear that, with the restrictions of (3.7), the quantum theory, like the classical, is only able to account for the normal triplet. It is, however, possible to generalize (3.5) empirically in such a way that the observations may be simply correlated, by writing for the term displacement

$$\triangle \nu = mg\triangle \nu_n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where g is the Landé "splitting factor," having a characteristic value, which may be expressed as a rational fraction, for each term.

The experimental study of "anomalous" line-splitting has led to two important generalizations. According to Preston's rule (1899) all the lines of the same series of an element undergo the same splitting in a magnetic field, as also corresponding lines of different elements. Runge's rule (1907) states that the separation of the components from the zero position (measured in frequencies) is a small multiple of an aliquot part of the "normal" separation. Preston's rule was established by extensive measurements of Runge and Paschen on the lines of Hg and allied elements, and on Mg, Sr and Ca; and Runge's rule appears to hold (at least in the ideal small field limit) except for complicated spectra such as that of neon. Preston's rule is of great importance in that it shows that there must be a close connection between the multiplet structure of lines and the Zeeman effect, and also that the Zeeman type, while depending on the azimuthal, is independent of the total quantum number of the combining terms.

The transverse effect is usually studied, as it is simpler experimentally, and all the components appear, while longitudinally only the ⊥ components are observed. Ideally, the splitting is symmetrical; in view of this and Runge's rule, the Zeeman pattern may be simply represented symbolically in a way which may be illustrated for the sodium D lines.

D_1 ($\lambda = 5{,}896$) and D_2 (5,890) constitute the first member of the principle series of sodium ($D_1 = 3s - 3p_1$, and $D_2 = 3s - 3p_2$), and their Zeeman pattern is typical of that of sp_1 and sp_2 lines generally in doublet series.

The Zeeman patterns are represented as follows:—

$$D_1 \ \frac{(2)\ \ 4}{3}$$

$$D_2 \ \frac{(1)\ \ 3\ \ 5}{3}$$

Parallel (∥) components are enclosed in brackets, and since the splitting is symmetrical, only the positively displaced components are indicated. The number below the line gives the Runge denominator, the numbers above give the numerators. The formulæ indicate that D_1 in a magnetic field splits up into 4 components, D_2 into 6.

$$D_1\begin{cases} \parallel & \Delta\nu = \pm \frac{2}{3}\Delta\nu_n \\ \perp & \Delta\nu = \pm \frac{4}{3}\Delta\nu_n \end{cases}$$
$$D_2\begin{cases} \parallel & \Delta\nu = \pm \frac{1}{3}\Delta\nu_n \\ \perp & \Delta\nu = \pm \frac{3}{3}\Delta\nu_n,\ \pm \frac{5}{3}\Delta\nu_n. \end{cases}$$

When there is no field, the undivided line is unpolarized; and when a field is applied, unless there are disturbing conditions, the sum of the intensities of the ∥ is equal to that of the ⊥ components. Every Zeeman type is characterized not only by its separations, but also by its intensity pattern.

As a further example of a Zeeman type, the diffuse triplet pattern ($d \longrightarrow p$, corresponding to a transition involving a change in the azimuthal quantum number from 3 to 2) as it occurs in Mg, Ca, etc., may be given. The natural "triplet," with the satellite lines, has actually six components, and these are split up in the following manner—

$$p_0d_1 \ \frac{(0)\ \ 1}{2} \qquad\qquad p_1d_2 \ \frac{(0)\ \ (2)\ \ 5\ \ 7\ \ 9}{6}$$

$$p_1d_1 \ \frac{1\ \ (2)\ \ 3}{2} \qquad\qquad p_2d_2 \ \frac{(2)\ \ (4)\ \ 5\ \ 7\ \ 9\ \ 11}{6}$$

$$p_2d_1 \ \frac{(0)\ \ 1\ \ (2)\ \ 3\ \ 5}{2} \qquad\qquad p_2d_3 \ \frac{(0)\ \ (1)\ \ (2)\ \ 6\ \ 7\ \ 8\ \ 9\ \ 10}{6}$$

Experimentally it is the splitting of the lines which is important; theoretically that of the terms, which may be deduced. It should be noted, however, that it is only from a consideration of the simpler term-splitting that it has been possible to push forward fruitfully the experimental investigation of the more complicated types of line-splitting.

2. Outline of Experimental Methods

The whole range of spectroscopic technique is involved in the study of the Zeeman effect; here only a few features will be referred to which are characteristic of the particular nature of the experimental problem. The normal separation of the Zeeman components is small; from (1.1), for $\lambda = 6{,}000$, and $H = 35{,}000$ gauss, $\triangle\lambda_n = {\cdot}60$ A.U., while for complicated Zeeman types, the separations may be very much less than this. A field greater than 40 KG cannot readily be obtained, and even if it could, its use would be limited in the study of the ordinary "weak field" splitting, owing to the distortion of the Zeeman pattern in strong fields due to the Paschen-Back effect. On the one hand, the spectral apparatus must be of high resolving power, and on the other, the sources must be such as to give spectral lines as narrow as possible.

The resolving power $\left(\frac{\lambda}{d\lambda}\right)$ necessary to separate the components may readily be calculated for different Zeeman types, assuming the lines to be indefinitely narrow. The fact that a resolving power of 1,000 just separates the D lines enables the significance to be appreciated of the numbers for some typical lines given in the following table, derived from Back,

Element and λ.	Spectral type.	r.	Zeeman type.	$d\lambda_{\text{min.}}$	$\left(\frac{\lambda}{d\lambda}\right)_{\text{min.}}$
Na 5,889·96	sp_2	2	$\frac{(1)\ 3\ 5}{3}$	·386	15,300
5,895·93	sp_1	2	$\frac{(2)\ 4}{3}$		
Ba 5,853·70	d_1f_2	3	$\frac{(0)\ (1)\ 3\ 4\ 5}{6}$	·094	62,340
Cd 3,610·51	p_2d_3	3	$\frac{(0)\ (1)\ (2)\ 6\ 7\ 8\ 10}{6}$	·036	100,900
Mn 4,033·07	sp_3	6	$\frac{(2)\ (6)\ (10)\ 60\ 64\ 68\ 72\ 76}{35}$	·031	132,000

TABLE XXIII.—ZEEMAN TYPES AND RESOLVING POWERS REQUIRED ($H = 35{,}000$).

for a field of 35,000 gauss. The term combination and multiplet class to which the line belongs ($r = 1, 2, 3 \ldots$ singlets, doublets, triplets) are indicated.

The space between the poles of the magnet in which a strong and uniform field can be maintained is usually cylindrical with axial length about 4 and diameter about 8 mm. The most generally useful form of source from the point of view of space requirements, intensity of light, and simplicity, is the spark in air. Geissler tubes give lines of high homogeneity. If, however, they are placed parallel to the field, the poles of the magnet must be bored, which disturbs the uniformity of the magnetic field, and decreases its intensity; while if placed at right angles, the field exerts a strong disturbing influence on the moving charges; not only is the life of the tube short, but Stark, pressure and temperature effects arise which decrease the homogeneity of the lines emitted. An arc does not work well at right angles to the field. Special arrangements, however, enable short arcs parallel to the field to be produced, and the vacuum arc is normally employed as a special form of source for securing high homogeneity of lines.

For the production of a spark in air, the lamellar electrodes may be attached to the pole pieces, covered by insulating strips. The leads are inclined at 90° to each other, and at 45° to the axis of observation. If the element under investigation is metallic, it may be used directly for the electrodes, or it may be alloyed with another metal which is not readily affected by the air. For some elements carbon electrodes, impregnated with a salt solution, may be employed. Even for metallic elements which can be used directly, carbon electrodes often yield better results. An alloy of the metal under investigation (e.g. Na, Zn, Cu, Al, etc.) with silver is produced by a reduction of mixed salts (e.g. $NaNO_3$ and $AgNO_3$) on the carbon electrode itself.

With metallic electrodes, using currents to give a reasonable intensity, the vapour pressure in the spark may become sufficiently great to produce considerable widening and self-reversal of the lines. With the silver-alloy carbon electrodes (the content of the metal investigated in the alloy being under control) it is possible to arrange conditions so that the lines obtained are both sharp and intense.

A vacuum arc arrangement of great efficiency has been developed by Back. The magnet pole pieces are fitted into a cylinder of brass, provided with " windows " and inlet tubes for the electrodes; the whole may be placed between the poles of the electromagnet. The enclosed inter-pole region may then be evacuated. One of the electrodes is capable of a slight to-and-fro "trembling" motion, controlled by a motor, so that an interrupted arc is produced, the heating effects thereby being lessened. The use of rubber rings enables small adjustments to be made in the interpole distance. The arc is maintained in the central strong homogeneous region of the field. Metals investigated can sometimes be used directly in the form of strips as electrodes, but special treatment is generally necessary, such as melting on to copper (Na, Tl, Pb, Sn) or manganese (Bi). Carbon electrodes are sometimes useful. The same apparatus can be adapted to the study of gas spectra, using pure, unimpregnated "glowed" carbon electrodes, or copper electrodes of special form. The noteworthy features of the arrangement, independently of its range of adjustment, are the very small interpole distances (some 3½ mm.) required, and the fact that the conditions may be controlled so as to give lines of remarkable homogeneity. The effective resolution which may be reached with a vacuum arc is greater by a factor of the order of three compared with that obtainable with the spark in air; and the times of exposure necessary are quite comparable.

The main points to be taken into account in connection with the magnetic field—constancy, intensity and homogeneity of the field, and constancy of temperature—have already been considered (Ch. III). In ordinary Zeeman-effect investigations it is unnecessary to measure the field directly, as it may be determined from the splitting of standard lines. Standard lines should not have too short a wave-length, the Zeeman separation should be large, and there should be more than three components, and the line should arise from a combination of terms of small azimuthal quantum number. These conditions, necessary to ensure that $\delta\lambda$ shall be large, that errors in measurement may be minimized, and that the lines shall be sharp, are well fulfilled by the first members of the sharp series triplets ($s \rightarrow p$ lines) of Zn and Cd.

It may be useful to give particulars of these :—

Zn.	Cd.	Zeeman type.
4,810·71	5,086·06	$\frac{(0)\ (1)\ 2\ 3\ 4}{2}$
4,722·34	4,800·09	$\frac{(1)\ 3\ 4}{2}$
4,680·38	4,678·37	$\frac{(0)\ 4}{2}$

TABLE XXIV.—Zeeman Standard Lines (Field "Normals").

The high resolving power necessary in the spectral apparatus will be clear from Table XXIII. A Rowland grating with many lines ($>$ 100,000) is by far the most generally useful. In the third or fourth order the resolving power is high, and the interpretation of the Zeeman patterns is direct. Interference spectroscopes may surpass the grating in resolution, and in light-gathering power; but there are usually compensating disadvantages. With the Michelson interferometer the interpretation of the results is uncertain; the superposition of different orders with an échelon makes it almost impossible to deduce the basic Zeeman pattern in complicated cases. With a Fabry-Perot étalon, or crossed Lummer-Gehrke plates, the results may, however, be more readily interpreted, and the enormous resolving powers which can be reached (up to 800,000) make these instruments a valuable aid in the study of special problems.

A minimum width for spectral lines is fixed by the Doppler effect. The change in wave length due to a velocity v of the molecules is given by

$$\delta\lambda = \lambda\frac{2v}{c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where

$$\overline{v^2} = \frac{3RT}{M} \doteqdot \frac{2{\cdot}49 \times 10^8 T}{M} \quad . \quad . \quad . \quad . \quad (7.1)$$

The width will thus be greater the greater λ, and the less the atomic weight of the element, which is one reason for the use of lines of an element of fairly high atomic weight (as Cd 112·4, Table XXIV) as field normals. With increasing azimuthal quantum number of the combining terms, the lines are less sharp, and the components in the Zeeman pattern closer, so that their resolution becomes more difficult. With a vacuum arc source, the Doppler width may be so small that, as an example, two lines of Al II—4,347·802 and 4,347·785—were resolved in the second order with a Rowland grating, corresponding to a resolving power of $2{\cdot}5 \times 10^5$, the theoretical resolving power being $2{\cdot}2 \times 10^5$.

Unless the resolution is sufficient, owing to the "fusion" of the Zeeman components, the Zeeman type may be completely misinterpreted. In complicated cases when the components are close, owing to the feeble intensity of some of them, the patterns are liable to be misinterpreted even when the resolving power is adequate. The analysis of the patterns is rendered more difficult by the fact that distortion usually occurs, the separations no longer being simple multiples of Runge fractions, owing to the Paschen-Back disturbances. The analysis has, however, been much simplified by Back's classification of the patterns into seven distinct fundamental Zeeman types, each of which has a characteristic appearance due to the sequence of intensities among its components. (Three of these types correspond to odd multiplicities, three to even, and one—a simple triplet—to odd or even.) Once the type is recognized, the " ideal " Runge fractions can be deduced from the separations of definite components; some of these remain unaltered whatever the strength of the field, while others give the " ideal " value in the mean. It is then possible to deduce the term components, combinations between which give rise to the observed line components.

It is beyond the scope of this book to enter into details as to experimental procedure, or the mode of analysing the results, for which reference must be made to the full account by Back. It has, however, seemed worth while to give some indication of what is involved not only in making observations, but also in setting forth the results in a form which is theoretically significant. It is the changes of energy of individual atomic levels (the term-splitting) under the influence of a magnetic field which are of theoretical interest; and it is this term-splitting with which the next section is concerned. In this section the Zeeman effect has been considered from an experimental standpoint, but it must be noticed that it is only by the continual mutual interaction of theory and experiment that the extraordinarily complicated phenomena have been analysed and co-ordinated. Experiment alone is as incapable of revealing the " nature of things " without theory, as is theory without experiment.

3. The Correlation of the Observations

A vigorous attempt was made by Voigt (1913) to extend the Lorentz theory to an anomalous effect of the sodium D line type, by making special assumptions as to the " coupling " between the electrons giving rise to the D_1 and D_2 lines. This theory was given a quantum translation by Sommerfeld, which enabled the splitting of doublets both in weak and strong fields to be formally accounted for. The extension of the results to multiplets generally is mainly due to Landé. Assumed structures of the atom based on the usual quantum-theory postulates have been of service in suggesting the kinds of relations to be anticipated, but as yet it has proved impossible to deduce the experimentally correct relations as resulting from the properties which the atoms would naturally be supposed to possess. For the present, physical interpretation will be largely left aside; but it is helpful to have a rough physical picture. As an emitter of spectral lines an atom may be regarded as composed of a core and a series electron. The quantum theory suggests that the electron orbit and the core will only be able to assume certain discrete relative orientations, and the atom as a whole definite discrete orientations relative to an external field. As long as the field is weak, the core-orbit orientations will be unaltered, but if it is strong, the core and orbit will orientate separately. The natural multiplet arises from the different energies corresponding to different core orbit orientations. It is the relative strength of the external to the "internal" field which decides whether it is to be regarded as strong or weak, and a field may be regarded as strong when the corresponding Larmor separation becomes comparable with the separations of the natural multiplet. In a weak field the atom may be treated as a single whole, with an angular momentum j, which is the vector sum of contributions from the core and series electron. Correspondence principle reasoning suggests that in an emission or absorption transition j can only change by 0 or 1 and the j's are actually so chosen that a selection principle of this kind is satisfied. This gives no indication of the absolute values of the j's, for which various values are favoured by different theorists (corresponding j's differing by the same amount). As far as the correlation of results is concerned, there is little to choose. Here the classification of Sommerfeld will be adopted, as this seems to have come into the widest use.

The spectral terms may, then, be classified by assigning to them a total quantum number n, an azimuthal quantum number k, and an inner quantum number j; the terms being differentiated by their inner quantum numbers when there is more than one energy level corresponding to a given nk. Using r to indicate the "permanent" term multiplicity (the terms with the smaller k's usually do not have the full number of components) the j values assigned by Sommerfeld are given in the following table.

Type of Term.	$k \diagdown r$	1	3	5	2	4
s	1	0	1	2	$\frac{1}{2}$	$\frac{3}{2}$
p	2	1	2 1 0	3 2 1	$\frac{3}{2}$ $\frac{1}{2}$	$\frac{5}{2}$ $\frac{3}{2}$ $\frac{1}{2}$
d	3	2	3 2 1	4 3 2 1 0	$\frac{5}{2}$ $\frac{3}{2}$	$\frac{7}{2}$ $\frac{5}{2}$ $\frac{3}{2}$ $\frac{1}{2}$

TABLE XXV.—j VALUES (SOMMERFELD).

The term components may be distinguished by writing the inner quantum numbers as subscripts, triplet p terms being indicated by p_0, p_1, p_2. For even series $\frac{1}{2}$ is added to the j value for convenience, giving p_1 and p_2 for the p doublet terms.

Transitions normally occur for which

$$\begin{aligned}\triangle k &= \pm 1\\ \triangle j &= \pm 1 \text{ or } 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)\end{aligned}$$

In a magnetic field each nkj term splits up into $2j + 1$ equidistant components. ($2j + 1$ gives the "statistical weight" of the term—see the discussion on electron distribution in atoms, Ch. V, sect. 2.) The separation of these from the original position in a magnetic field is given by—

$$\triangle\nu = mg\triangle\nu_n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (9)$$

m (which may be regarded as the resolved value of j) takes the values j, $j - 1$, $j - 2$ . . . $-j$ for each j term (and hence is integral for odd, and half integral for even multiplets), and g, the Landé "splitting factor," may be written as

$$g = \tfrac{3}{2} + \frac{\left\{\frac{r}{2} - (k - \frac{1}{2})\right\}\left\{\frac{r}{2} + (k - \frac{1}{2})\right\}}{2j(j + 1)} \quad . \quad . \qquad (10)$$

(8), (9) and (10), in conjunction with (1)–(5), then cover completely the observations on the Zeeman effect in a weak magnetic field for ordinary spectra. The mg values for multiplicities up to 4 are shown in Table XXVII (based on that of Landé). A single example will be sufficient to show how they lead to the observed line types. In the following scheme for the D lines the dotted transitions ($\triangle m = 0$) give the ∥ components—

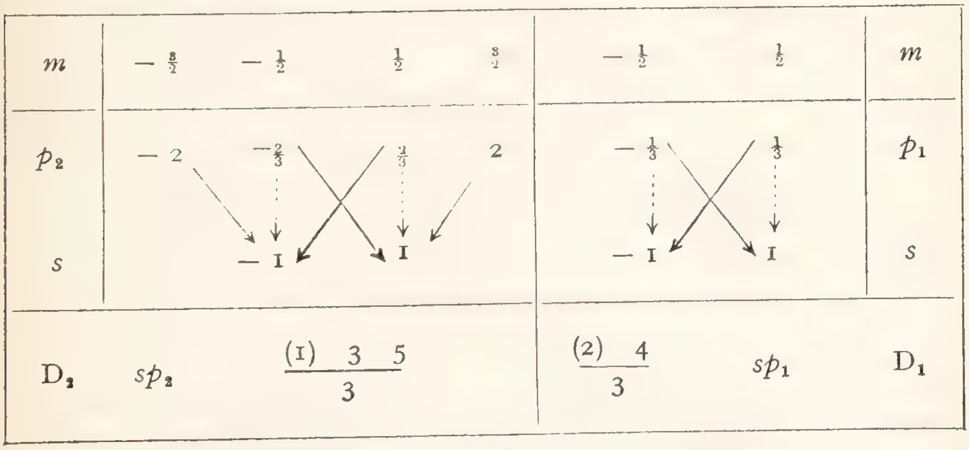

TABLE XXVI.—D-line Zeeman Transitions.

$r = 2$ $\quad s \quad m = \pm\frac{1}{2} \qquad g = 2 \qquad j = \frac{1}{2}$

$\qquad\qquad p_1 \quad m = \pm\frac{1}{2} \qquad g = \frac{2}{3} \qquad j = \frac{1}{2}$

$\qquad\qquad p_2 \quad m = \pm\frac{3}{2}, \pm\frac{1}{2} \qquad g = \frac{4}{3} \qquad j = \frac{3}{2}$

Sommerfeld regards j as the resultant of the vector addition of j_s due to the core and j_a due to the series electron, j_s and j_a being given by

$$j_s = \tfrac{1}{2}(r-1) \qquad j_a = k - 1 \quad . \quad . \quad . \qquad (11)$$

j_s and j_a are compounded in every way which gives integral (for odd multiplicities) or half-integral resultants (for even multiplicities), so that, in particular, $j_{\max} = j_s + j_a$ and $j_{\min} = |j_s - j_a|$. It may be noted that, from (11), for s terms, $j = j_s = \frac{1}{2}(r-1)$.

In strong fields the g values of (10) no longer apply. The "complete" Paschen-Back effect occurs when the core and electron orbit orientate separately; the g values are then all integral and the separations, according to Pauli, are given by

$$\frac{\triangle\nu}{\triangle\nu_n} = \begin{cases} m + j - j_a & \text{for } m \geqq j_s - j_a \\ 2m + j - j_s & \text{for } m \leqq j_s - j_a \end{cases} \quad . \quad . \qquad (12)$$

The separations are, however, no longer to be measured from each individual term component, but approximately from the "centre of gravity" of the whole set of j components of the nk term considered. Then, in virtue of the restriction (3.7) the multiplet as a whole gives rise simply to a "normal" triplet.

In general, if ν_s is the frequency corresponding to the centre of gravity of the term components, for any particular component

$$\nu = \nu_s + \gamma\delta\nu + mg\triangle\nu_n \quad . \quad . \quad . \quad . \quad . \qquad (13)$$

where $\delta\nu$ is a constant depending on the separations of the components of the natural multiplet (e.g. for doublet p terms, for p_1, $\gamma = -\frac{2}{3}$, for p_2, $\gamma = +\frac{1}{3}$). Both γ and g are functions of the applied field. Landé has made some tentative generalizations as to the changes in γ, but they will not be considered here. The g values for weak fields are given by (10), and for strong (with less experimental support) by (12). (In 12 actually the mg values are given.) Pauli arrives at (12) partly by generalization, on a pseudo-model basis, of the Voigt-Sommerfeld results for doublets, and partly by the use of an important principle as to the "permanence" of g sums, Σg or Σmg, taken over all the j's, for fixed values of r, k, and m, being the same for any field strength. This has been experimentally confirmed, and indeed lies at the basis of Back's analysis of line types. In Table XXVII the limiting strong-field mg values are given on the right of those for weak fields, and it will be seen that the $\Sigma mg_{\text{weak}} = \Sigma mg_{\text{strong}}$ principle is satisfied. That Σg has an important theoretical significance seems highly probable, as it is found to satisfy simple relations even for complicated spectra of the neon type. The significance, however, is not yet clear.

Summarizing, it may be said that the rules and relations, given in this section, while not striking for their simplicity, are yet far simpler than the observational results which they serve to correlate. The apparent necessity for the introduction of half quantum numbers, however, does not fit in harmoniously with the ordinary quantum theory ideas, and it will be seen that attempted physical interpretations reveal further remarkable anomalies. The schemes must be regarded as constituting no more than a scaffolding on which adequate theories may eventually be built up.

k	$j \backslash m$	-2		-1		0		1		2	
1	0					0	0				
2	1			-1	-1	0	0	1	1		
3	2	-2	-2	-1	-1	0	0	1	1	2	2

Singlet Terms. $r = 1$.

k	$j \backslash m$	$-\frac{5}{2}$		$-\frac{3}{2}$		$-\frac{1}{2}$		$\frac{1}{2}$		$\frac{3}{2}$		$\frac{5}{2}$	
1	$\frac{1}{2}$					-1	-1	1	1				
2	$\frac{3}{2}$			-2	-2	$-\frac{2}{3}$	0	$\frac{2}{3}$	1	2	2		
	$\frac{1}{2}$					$-\frac{1}{3}$	-1	$\frac{1}{3}$	0				
3	$\frac{5}{2}$	-3	-3	$-\frac{9}{5}$	-1	$-\frac{3}{5}$	0	$\frac{3}{5}$	1	$\frac{9}{5}$	2	3	3
	$\frac{3}{2}$			$-\frac{6}{5}$	-2	$-\frac{2}{5}$	-1	$\frac{2}{5}$	0	$\frac{6}{5}$	1		

Doublet Terms. $r = 2$.

k	j \ m	-3		-2		-1		0		1		2		3	
1	1					-2	-2	0	0	2	2				
2	2			-3	-3	$-\frac{3}{2}$	-1	0	1	$\frac{3}{2}$	2	3	3		
	1					$-\frac{3}{2}$	-2	0	0	$\frac{3}{2}$	1				
	0							0	-1						
3	3	-4	-4	$-\frac{8}{3}$	-2	$-\frac{4}{3}$	0	0	1	$\frac{4}{3}$	2	$\frac{8}{3}$	3	4	4
	2			$-\frac{14}{6}$	-3	$-\frac{7}{6}$	-1	0	0	$\frac{7}{6}$	1	$\frac{14}{6}$	2		
	1					$-\frac{1}{2}$	-2	0	-1	$\frac{1}{2}$	0				

Triplet Terms. $r = 3$.

k	j \ m	$-\frac{7}{2}$		$-\frac{5}{2}$		$-\frac{3}{2}$		$-\frac{1}{2}$		$\frac{1}{2}$		$\frac{3}{2}$		$\frac{5}{2}$		$\frac{7}{2}$	
1	$\frac{3}{2}$					-3	-3	-1	-1	1	1	3	3				
2	$\frac{5}{2}$			-4	-4	$-\frac{12}{5}$	-2	$-\frac{4}{5}$	0	$\frac{4}{5}$	2	$\frac{12}{5}$	3	4	4		
	$\frac{3}{2}$					$-\frac{39}{15}$	-3	$-\frac{13}{15}$	-1	$\frac{13}{15}$	1	$\frac{39}{15}$	2				
	$\frac{1}{2}$							$-\frac{4}{3}$	-2	$\frac{4}{3}$	0						
3	$\frac{7}{2}$	-5	-5	$-\frac{25}{7}$	-3	$-\frac{15}{7}$	-1	$-\frac{5}{7}$	1	$\frac{5}{7}$	2	$\frac{15}{7}$	3	$\frac{25}{7}$	4	5	5
	$\frac{5}{2}$			$-\frac{120}{35}$	-4	$-\frac{72}{35}$	-2	$-\frac{24}{35}$	0	$\frac{24}{35}$	1	$\frac{72}{35}$	2	$\frac{120}{35}$	3		
	$\frac{3}{2}$					$-\frac{9}{5}$	-3	$-\frac{3}{5}$	-1	$\frac{3}{5}$	0	$\frac{9}{5}$	1				
	$\frac{1}{2}$							0	-2	0	-1						

Quartet Terms. $r = 4$.

TABLE XXVII.—*mg* VALUES IN STRONG AND WEAK FIELDS. The strong and weak field values are separated by the dotted lines, the weak field value being given first.

4. Spectroscopic Magnetic Moments

If the mechanical and magnetic moment of an atom are not invariably related by the equation $\mu = \frac{e}{2mc}j$, it is not possible to state a priori whether *mg* in (9) is a measure of the mechanical or of the magnetic moment—or, indeed, of either. The Gerlach and Stern experiments do, however, seem to justify the assumption, which has generally been made tacitly, that the *mg* values deduced from the Zeeman effect actually give the possible values for the resolved magnetic moment of the atom in a given state in the direction of the applied field. (The magnetic moment is supposed expressed as a multiple of the Bohr unit.)

Referring to Table XXVII, for doublet atoms in an *s* state $mg = \pm 1$. For Cu, Ag, Au, $\mu = \pm 1$. These atoms give rise to doublets, and in their normal unexcited state, the series electron moves in an *s* orbit. Zn, Ca, Hg are normally in a singlet S state with $mg = 0$ (correspondingly $\mu = 0$). Tl gives traces corresponding to $\mu = \pm \frac{1}{x}$ where $x \doteqdot 3$. If normally it is in a doublet p_1 state, which is probable, this again is in agreement with the *mg* values. In general, an atom in an *s* state, which gives rise to spectra of multiplicity *r*, should give, in the Gerlach and Stern experiment, *r* traces at separations corresponding to $\mu = 2$; for uneven multiplicities there should be an undisplaced trace, as is actually observed for Ni.

The connection between the type of spectrum emitted by an atom and its magnetic moment enables some interesting conclusions as to the sequence of magnetic properties of atoms in proceeding across the periodic table to be drawn from the sequence in the types of spectra. The elements K–Cu have been investigated most fully. Observed multiplicities are shown in the following table :—

Element	K	Ca	Sc	Ti	V	Cr	Mn	Fe
Atomic Number Z . .	19	20	21	22	23	24	25	26
(Z − 18) − 1	0	1	2	3	4	5	6	7
Observed Multiplicities *r*	2	$\underline{1}$ 3	$\underline{2}$ 4	1 $\underline{3}$ 5	$\underline{4}$ 6	5 $\underline{7}$	4 $\underline{6}$ 8	3 $\underline{5}$ 7

TABLE XXVIII.—Observed Multiplicities (*r*).
(The most strongly developed are underlined.)

(Z − 18) − 1 gives the number of electrons the core contains in addition to those in the closed argon configuration. The equations on which Table XXVII, for multiplicities up to 4, is based, enable the possible resolved magnetic moments of the atoms to be determined for any of the states corresponding to a definite value of r; in particular, for the normal unexcited state, if this is known. Thus, for K, Ca, Cr and Mn, the ground terms are *s* terms, of doublet, singlet, septet, and sextet systems, the corresponding normal moments being 1, 0, 6 and 5 respectively; Fe has a quintet *d* term, and Ti and V apparently have *f* terms as ground terms.

From a model point of view, the atom has its maximum magnetic moment when the moments of the core and series electron are in the same direction. The maximum moments, which are then the same whether the field is weak or strong, are given in the next table:—

Multiplicity r.		1	2	3	4	5	6	7
Term type.	s $(k = 1)$	0	1	2	3	4	5	6
	p $(k = 2)$	1	2	3	4	5	6	7
	d $(k = 3)$	2	3	4	5	6	7	8

TABLE XXIX.—MAXIMUM MAGNETIC MOMENTS.

It is natural to suppose (cf. V, 23) that the maximum moment due to the series electron is given by k. If this is so, the magnetic moment of the core (μ_c) corresponding to any multiplicity can at once be deduced.

r	1	2	3	4	5
μ_c	-1	0	1	2	3

Magnetic moment of core.

μ_c is in fact given by

$$\mu_c = r - 2 \tag{14}$$

while for an atom in any k state the maximum moment is given by

$$\mu_{\max} = \mu_c + k = r + k - 2 \tag{15}$$

It will be seen at once, from Table XXVIII, that (14) fits in harmoniously with the observed facts. For a doublet atom $\mu_c = 0$. In agreement with this, K has a core with the diamagnetic argon configuration. The Ca core contains 1 electron external to a completed configuration. According as this rotates in the same direction as the series electron or the opposite $\mu_c = 1$ or -1. Let n_c be the number of electrons the core contains in addition to those in the completed configuration. (For the elements in Table XXVIII, $n_c = (Z - 18) - 1$.)

Then, in general

$$\mu_c \ngtr n_c.$$

It appears as if the maximum contribution of the n_c electrons to the core moment is n_c; and that these electrons may balance in pairs, giving rise to core moments smaller by 2, 4 . . . so that the multiplicities observed in virtue of (14) are all odd or all even, according as n_c is odd or even. The maximum multiplicity is greater by one than the total number of electrons in the atom in addition to those in closed configurations. The fact that different multiplicities are observed for the same atom shows that the core can assume different magnetic states, the relative probability of which will depend on the temperature and other conditions.

Leaving aside developments of these views which apply more particularly to spectral theory, it is of interest to compare the spectroscopic core magnetic moments with those deduced for ions from the magneto-chemical measurements. Although, in the production of spectral lines, quantum transitions of more than one electron may sometimes be involved (this is probably so in transitions involving ordinary and "dashed" terms) normally the lines are due to transitions of a single series electron between states in which it is much more loosely bound than any of the other electrons in the atom. The core may then be regarded as constituting a simple system, stable and unaltered in an applied field. The striking point which emerges from the above discussion is that such a core, as a whole, may be characterized by an integral magnetic moment (suggesting that non-integral moments are found when a "compound" system is involved, when there is no sharply differentiated series electron—simple and compound being, of course, purely relative terms). Although a core may be supposed to have a constitution somewhat similar to that of an ion with the same number of electrons, invariable and complete similarity would not be expected, for the nuclear charge will generally not be the same, while the temperature and other conditions will differ widely for ions in solutions or solid salts and for cores in atoms being excited to give spectra. It is, however, natural to compare core and ionic moments. Possible moments for cores containing $Z - 1$ electrons may be deduced from Table XXVIII by subtracting 2 from the numbers there given for the multiplicities.

These values are plotted in Fig. 42, together with the values obtained for ions from the magneto-chemical measurements, given in Table XX, and discussed in Chapter VII, section 2.

On the left-hand side of the figure the ionic moments agree well with possible core moments. Co^2 25 with an ionic moment of 4 is anomalous, as the spectra would indicate an uneven moment. There is, however, the possibility that there may be an equilibrium between ions in different magnetic states.

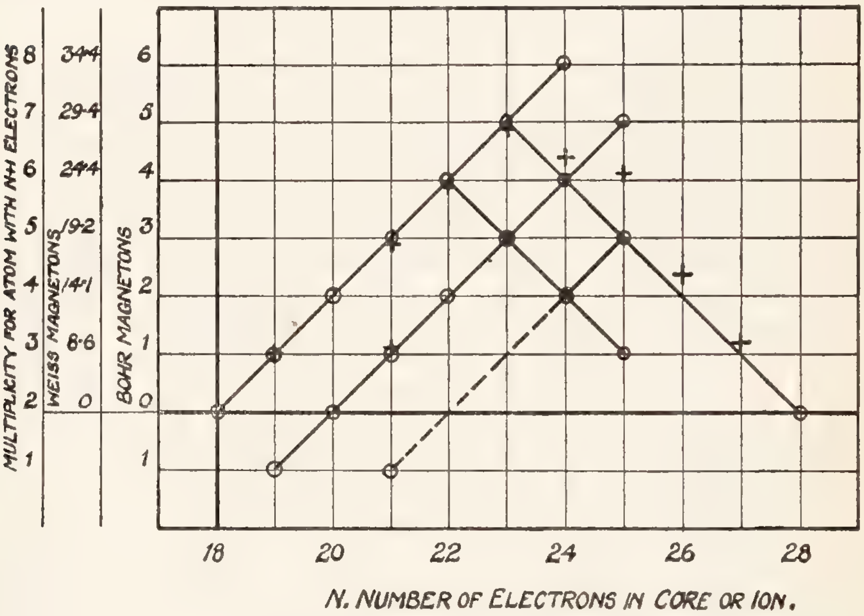

FIG. 42.—Magnetic Moments of Cores and Ions.

⊙ Magnetic moment of core from spectra.
+ Magnetic moment of ion.

In deducing the Weiss p value for an ion with a given integral magnetic moment, the assumption at the basis of Sommerfeld's treatment (Ch. VII, sect. 1, equation 4.3) was that the ion orientated itself similarly to an atom in an s state. It has already been suggested that this may have some justification, if ions may be regarded as "simple systems"; for atoms in an s state also behave as simple systems, in that, as will be seen from Table XXVII, their resolved moments are always integral, and are the same in strong and weak fields. This may account for the agreement in the observed and calculated p values for the simpler ions; the more complex ions, however, do not seem to behave in accordance with this scheme.

Following an argument similar to that already given (Ch. VII, sect. 1, equation 3.1), the Weiss magneton value corresponding to any *nkj* state of an atom is given approximately by

$$p = 5\sqrt{3\overline{(mg)^2}} \quad . \quad . \quad . \quad . \quad . \quad (16)$$

(As an example, for a triplet atom in an s state ($k = 1$), from Table XXVII, $mg = -2$, 0 or 2, giving $p = 5\sqrt{8} \doteq 14{\cdot}2$.) Quite generally, adopting Sommerfeld's j classification, and noting that m assumes the values $j, j-1, j-2 \ldots -j$, (16) may be written in the form

$$p = 5gj\sqrt{\frac{j+1}{j}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Tamm has applied this expression to the calculation of ionic moments, assuming that the ions behave magnetically like *atoms* with the same number of electrons in an *nkj* state which may differ from an s state. The p value corresponding to any k^r_j state can be calculated from (17); and if this agrees with the value found experimentally, it might be taken to give some indication of the normal state of the ion. The method is illustrated by the following figures :—

Ion	Fe^2 24		Co^2 25		Ni^2 26	
p obs.	26		24·5		16	
p calc.	$s^5_2\ d^7_2$ d^5_3 p^7_2	24·5 26·0 28·6	$p^4_{5/2}$ $p^6_{5/2}$ $d^6_{5/2}$	23·7 26·2 24·5	d^3_2 p^5_1	14·3 17·7

TABLE XXX.—OBSERVED IONIC MOMENTS AND CALCULATED ATOMIC MOMENTS.

The numbers suggest that for ions and atoms with the same number of electrons (Tamm) the normal state of Fe^2 may be similar to the d_3 state of a quintet atom with 24 electrons, of Co^2 to $d_{5/2}$ of a sextet atom and so on. This would indicate that in the Fe^2 and Co^2 ions in their normal state the most loosely bound electrons are moving in a $k = 3$ orbit, which is exactly what would be expected on the quantum theory of atomic structure (Ch. V, sect. 2). In general, however, calculated magneton values do not agree so closely with those observed, notably for Fe^3 and Ni^2; though for Ni^2, g^5_3 (corresponding to

$k = 5$ for the most loosely bound electron in the ion) gives $p = 15 \cdot 9$.

This method of attack on the ionic moment problem is certainly on reasonable lines, though at present the treatment is very arbitrary, and any theoretical-experimental agreement obtained must be regarded as rather fortuitous. Little further progress can be made until the spectra have been more fully analysed, on the lines suggested by recent work (see Ch. XIV, sect. 1), and the normal states of atoms with a given number of electrons determined. Even then, it seems improbable that the electronic constitution of an ion will be the same as that of an atom with different nuclear charge (e.g. Ni^2 26 and Fe 26). These difficulties are independent of those already discussed connected with the indefiniteness of some of the ionic moments themselves.

In the correlation of ionic and spectroscopic magnetic moments the goal has not yet been reached, but it is being rapidly approached. Much progress has been made. Amongst the wealth of detail, there is a liability to lose sight of the astounding fact that from experiments so diverse as those on susceptibilities of salts and solutions, on the magnetic deviation of atomic rays, and on the multiplet structure of spectral lines, accordant conclusions may be drawn as to the magnetic moments of atoms and parts of atoms. Details are generally being fitted into a simple and coherent design, and in the process the quantum theory, which provided the key, is itself being refined and extended.

5. Intensity and Interval Rules

Intensity Rules.—A great deal of work has recently been done by Ornstein and his collaborators, notably Burger and Dorgelo, at Utrecht, on the relative intensity of the component lines of multiplets. They have found that some simple "summation rules" give results which are in remarkable accord with the experimental measurements.

Let P be the "statistical weight" of an nkj term. Then P gives the number of possible and equally probable ways in which the nkj state can be realized, as revealed by the number of magnetic components of the term. In the absence of an external field the energy of the P states is the same; but their separate individuality is shown by the fact that their energies are influenced differently by the field. Using Sommerfeld's j's

$$P = 2j + 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Consider a multiplet produced by transitions from an nk to an $n'k'$ term, the former having components j_1, j_2, . . . and the latter j_1', j_2', . . . Then the summation rules state that the sum of the intensities of the line components produced by transitions *from* j_1, j_2 . . . are proportional to P_{j_1}, P_{j_2} . . . ; and the sum of the intensities of components produced by transitions *to* j_1', j_2' . . . are proportional to $P_{j_1'}$, $P_{j_2'}$ . . .

When there is only a single final state (as in $p \longrightarrow s$ multiplets) the intensities are proportional simply to $2j + 1$ for the initial states. The relative intensities of the different sp components follow at once from Table XXV.

r.	Relative intensities.						
2				4		2	
3			5		3		1
4		6		4		2	
5	7		5		3		

The ratio 2 : 1 is found not only for the sodium D lines, but for the sp lines of alkalis generally, showing that, in agreement with the rules, the relative intensities are independent of the total quantum numbers. For the Cr quintet system triplet $\lambda = 5{,}208$, $5{,}206$, $5{,}204$, with the calculated ratio $7 : 5 : 3 = 100 : 71{\cdot}4 : 42{\cdot}9$, measurement gave $100 : 72 : 45$.

The next simplest case is provided by pd combinations in a doublet system. The transitions giving the principal lines, intensities a and b, and the satellite c are shown, with the j values of the initial and final states.

		d	
		$\frac{5}{2}$	$\frac{3}{2}$
p	$\frac{3}{2}$	a	c
	$\frac{1}{2}$		b

Since $P = 2j + 1$, the summation rules yield the equations

$$a + c : b = 4 : 2 \qquad b + c : a = 4 : 6$$

from which the relative values of a, b and c can be determined, giving a ratio $9 : 5 : 1 (= 100 : 56 : 11)$ which is in agreement with the values found experimentally for the Cs group 6,217, 6,213, 6,210 (100 : 60 : 12).

In general, for more complicated multiplets, the summation rules do not yield sufficient equations to determine the relative intensities uniquely. The correspondence principle, however, gives a *qualitative* indication of the intensities, as has been shown by Sommerfeld and Heisenberg, though it naturally gives no suggestion of whole-number rules. Assuming that the intensities are controlled by whole-number rules, in particular the summation rules, it is possible to build up, on the basis of the qualitative correspondence principle indications, intensity schemes which, although tentative, are quantitative and general (Sommerfeld and Hönl, Russell, Kronig). The predicted intensities agree very closely with those observed.

A similar procedure may be followed in predicting the intensities of Zeeman components—that is, the various $m \longrightarrow m'$ lines which appear separately when a field is applied, corresponding to the single $j \longrightarrow j'$ line in the absence of a field. Ornstein and Burger showed that in simple cases the intensities could be uniquely determined on the whole-number assumption combined with symmetry and polarization rules—the intensities of the ⊥ and ‖ components of the (ideal) Zeeman multiplet are symmetrical about the midpoint, and the sum of the intensities of the ⊥ is equal to that of the ‖ components. Their conclusions have been generalized by Hönl on a correspondence principle basis. As far as comparison is possible, the results are in agreement with the "ideal" Zeeman patterns deduced from the observations. In so far as the results are in accordance with the observations both on the $j \longrightarrow j'$ components of a natural $k \longrightarrow k'$ multiplet, or on the $m \longrightarrow m'$ Zeeman components of a given $j \longrightarrow j'$ line, the essentially significant point which emerges may be stated as follows: The number of actual quantum transitions occurring per unit time from each initial *kjm* state is the same; and the number of transitions to each final *k'j'm'* state is the same. (It should be noticed that the observed ratio of the intensities of ⊥ and ‖ components, in transverse observation, must be taken as half that of the number of corresponding transitions.) The probability of the transitions (the corresponding energies $h\nu$ being approximately the same for each) is thus independent of the quantum numbers defining the initial or the final state. On the one hand, this is in agreement with the attribution of an equal statistical weight (or a priori probability) to each separate *nkjm* state (see Ch. V, sect. 2); on the other with the quantum view that radiation is essentially a discontinuous process.

Interval Rules.—It has long been observed that the ratio of the separations of the components of a principle series triplet ($p \longrightarrow s$ in Mg, Ca, etc.) is approximately 2 to 1. Writing the inner quantum numbers of the p term components as subscripts, this may be expressed as

$$\Delta p_{01} : \Delta p_{12} = 1 : 2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

On a semi-model basis, Landé has deduced a general relation for the relative separations of the components of a multiplet term, of which (19) is a special case; if j and j' are the inner quantum numbers of the components considered, Landé's relation may be written

$$\nabla\nu_{jj'} \propto (j - j')(j + j' + 1) \quad . \quad . \quad . \quad . \quad (20)$$

For neighbouring components ($j - j' = 1$), writing $P = 2j + 1$ (as in (18)),

$$\Delta\nu_{jj'} \propto \tfrac{1}{2}(P_j + P_{j'}) \quad . \quad . \quad . \quad . \quad . \quad (20.1)$$

—the separation of the term components varies as the mean of their statistical weights. For terms of odd multiplicity the intervals are therefore in the ratio 2, 4, 6 . . . , for even terms 3, 5, 7 . . . (see Table XXV). While (20.1) gives ratios in close agreement with those found in many cases, in general the agreement is poor, as has been shown by Hicks from a large number of examples. Landé's interval rule is derived from the assumption that the differences in energy of the various j term components is due to the differences in the mutual *magnetic* energy of the series electron orbit and the core, owing to their varying relative orientation. It will be seen in the next section that the treatment is purely formal, and further that the purely magnetic theory leads to quite incorrect results for the *absolute* magnitude of the separations.

One of the most striking successes of the quantum theory was Sommerfeld's explanation of certain of the X-ray doublets as arising from the relativity change of mass of the series electron moving in its orbit. From V (12.1) and (14.1), for the difference in wave number of terms due to an electron moving round a charge Ne in orbits of the same total quantum number n, but different azimuthal quantum numbers, k, k'—

$$\Delta\nu_{kk'} = R\alpha^2 \frac{N^4}{n^3}\left(\frac{1}{k} - \frac{1}{k'}\right) \quad . \quad . \quad . \quad . \quad . \quad (21)$$

$$= 5{\cdot}84 \frac{N^4}{n^3} \frac{k' - k}{kk'} \quad . \quad . \quad . \quad . \quad . \quad (21.1)$$

Let Z be the atomic number, s the relativity screening constant. Then (21.1) becomes

$$\Delta\nu_{kk'} = 5{\cdot}84 \frac{(Z - s)^4}{n^3} \frac{k' - k}{kk'} \quad . \quad . \quad . \quad (21.2)$$

Putting $n = 2$, $k' = 2$, $k = 1$,

$$\Delta\nu_{kk'} = {\cdot}365(Z - s)^4 \quad . \quad . \quad . \quad . \quad . \quad (21.3)$$

With $s = 3{\cdot}5$, this formula gives, with close approximation, the $L_{II} - L_{III}$ separation throughout the whole range of elements investigated. Now the L_{II} and L_{III} levels are completely analogous to $2p_1$ and $2p_2$ optical doublet levels. These differ in their inner quantum numbers (and therefore, presumably, in the relative core-orbit orientation) but not in their azimuthal quantum numbers. While, therefore, doubt is cast on the validity of the relativity interpretation of the X-ray doublets, as at present formulated, it becomes reasonable to test whether a formula analogous to (21.2) fits optical doublet separations, and also multiplet separations generally.

Millikan's remarkable work on hot spark spectra has shown that atoms stripped of all but one valence electron such as Be II, B III, C IV, N V, and also the series Mg II, Al III . . . Cl VII (the Roman numerals indicate the resultant core charge) all give rise to doublet series; and that the $p \longrightarrow s$ doublet separations are given quantitatively by the formula (21.2) if an appropriate, but essentially reasonable, choice is made for the screening constant. Millikan has stressed the relativity-magnetic dilemma which this remarkable agreement indicates; in the formulæ it is necessary to put $k' = 2$ for the p_2 term, and $k = 1$ for the p_1 term, although the azimuthal quantum number of these terms is actually the same. Millikan has further shown that the relativity formula applies also to triplet terms for atoms stripped of all but two valence electrons, $k' = 2$ and $k = 1$ giving the separation of the outer components.

That a formula of the relativity type applies quite generally to multiplets for the whole range of elements, when a suitable choice of screening constants is made, has been shown by Landé, and also by Menzies, who has made use of the regularities revealed for the classification of lines of spectra whose series were hitherto doubtful. Landé considers that the separations of the doublet and outer triplet term components are most adequately expressed by the formula—

$$\triangle \nu = R\alpha^2 \frac{Z_a{}^2 Z_i{}^2}{n_a{}^3 k(k-1)} \quad . \quad . \quad . \quad . \quad (22)$$

Here Z_a is equal to the core charge (= 1, 2, 3 . . . for neutral, singly ionized, doubly ionized . . . atoms) and n_a is the "effective" total quantum number

$$\nu = \frac{RZ_a{}^2}{n_a{}^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22.1)$$

The series electron moves partly outside, and partly within the core; and Z_i is the effective charge round which it moves while describing the inner part of its orbit. $Z - Z_i = s$, the "inner" screening constant, which is approximately equal to 4 for all p terms except for elements in the first period where $s \doteq 2$. The formula (22) not only covers many qualitative regularities which have been observed—as to the variation of $\triangle\nu$ with core charge, with atomic number for elements in the same column of the periodic table, and with total quantum number for terms of given azimuthal number—but also with the relativity proportionality factor, gives the absolute intervals with close approximation. The physical interpretation of the formula will be shortly considered.

6. Attempted Physical Interpretations

Most of the attempts which have been made hitherto to derive theoretically the formulæ correlating the Zeeman effect observations have been based on such arbitrary assumptions, and have proved so unfruitful that they will only be briefly outlined. It has already been noted that Sommerfeld considers j as representing the angular momentum of the atom, compounded of a contribution j_s from the core and j_a from the series electron (see equation 11); the possible combinations of j_s and j_a giving integral and half-integral resultants (according as j_s is integral or half-integral) then determine the number of possible j components of each k term, together with the j values. The magnetic quantum number m is the resolved component of j in the direction of an applied field, while mg gives the resolved magnetic moment. Since m takes the values $j, j-1, j-2 \dots -j$, $mg_{\max}$, giving the magnetic moment of the atom, is equal to jg.

$$\mu = jg \qquad g = \frac{\mu}{j} \quad . \quad . \quad . \quad . \quad . \quad (23)$$

The Landé splitting factor (10) may be written in the form

$$g = 1 + \frac{j(j+1) + j_s(j_s+1) - j_a(j_a+1)}{2j(j+1)} \quad . \quad (24)$$

and the Landé interval formula (20) as

$$\triangle\nu_{jj'} \propto j(j+1) - j'(j'+1) \quad . \quad . \quad . \quad . \quad (25)$$

The only way in which it has been possible to derive a g formula bearing any resemblance to (24) is by assuming that the contribution of the core to the magnetic moment of the atom is twice as great as would be expected from its angular momentum. Let J, Js and JA be the actual angular momenta of the atom as a whole, of the core and of the series electron. J is the vector sum of J_S and J_A.

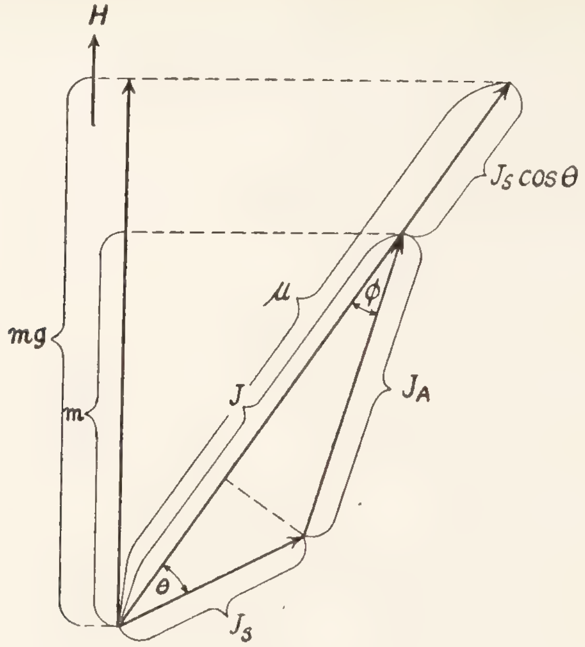

FIG. 43.

In accordance with the above assumption—

$$J = J_A \cos\phi + J_S \cos\theta \quad . \quad . \quad . \quad . \quad . \qquad (26{\cdot}1)$$

$$\mu = J_A \cos\phi + 2J_S \cos\theta \quad . \quad . \quad . \quad . \quad . \qquad (26.2)$$

$$\frac{\mu}{J} = 1 + \frac{J_S \cos\theta}{J}$$

$$\frac{\mu}{J} = 1 + \frac{J^2 + J_S^2 - J_A^2}{J^2} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (26.3)$$

This formula is somewhat similar to (24); the differences have led to the suggestion that in deriving the g formula it may be necessary to take into account two quantum states characterized by inner quantum numbers j and $j + 1$—an idea which has been developed by Heisenberg.

If the core and series electron each have a magnetic moment their mutual magnetic energy will be proportional to the cosine of the angle between their axes; if W represents this magnetic energy, and C is a constant

$$W = C \cos (J_S J_A)$$
$$= C\frac{J^2 - J_S^2 - J_A^2}{2J_S J_A}.$$

Thus, for the interval between the J and J′ components of a given k term (J_S and J_A constant),

$$\Delta\nu_{JJ'} \propto J^2 - J'^2 \quad . \quad . \quad . \quad . \quad . \quad . \qquad (27)$$

This formula bears the same relation to (25) as does (26.3) to (24).

A model treatment of the Paschen-Back effect is possible on the same lines; assuming a double magnetic effect for the core, g formulæ may be derived, bearing the same relation to the empirically correct formulæ as those for weak fields.

It may be said that practically all the changes reasonably possible in the assignment of inner quantum numbers to atoms, cores, and electrons have been rung in the attempts to derive theoretically formulæ agreeing with experiment; anomalies of a similar type are, however, always encountered—half-quantum number anomalies, magnetic core anomalies, and anomalies indicated by the necessities of substituting for the J's of the "model" formulæ means of two actual j's.

It has already been mentioned that j values are primarily so chosen as to give a satisfactory selection principle for possible transitions (8). One conclusion which, it seems, must be drawn from the failure of the theories is that their identification of inner quantum numbers with actual atomic angular momenta, though justifiable as a tentative procedure, does not lead to satisfactory results. There is no *direct* experimental evidence as to atomic angular momenta. Practically the only direct evidence available is that as to resolved atomic magnetic moments in the direction of an applied field. As has been discussed in section 4, the results are in agreement with the view that cores and electron orbits, considered alone, may be characterized by whole-number magnetic moments.

There seems little doubt that the different j states of an atom (k constant) do differ in the relative orientation of the core and series electron orbit, and following Heisenberg and Landé, an approximate calculation may be made as to the multiplet intervals to be expected if the difference in energy of the terms is due mainly to differences in magnetic energy of the core-electron system. From V (27), the magnetic field at the focus of an nk orbit for a single electron rotating round a charge Ne is given by

$$H = \frac{eh}{2\pi mc}\, k\left(\frac{N}{nka_H}\right)^3 \quad . \quad . \quad . \quad . \quad . \quad . \qquad (28)$$

where

$$a_H = \frac{h^2}{4\pi^2 e^2 m_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (28.1)$$

Let $\triangle m$ be the difference in the resolved magnetic moment of the core (in Bohr units) in the direction of H in two j states; the wave-number difference of the terms, due to the difference in precessional energy, will then be

$$\triangle\nu_{\text{mag}} = \frac{e\mathrm{H}}{4\pi m_0 c}\triangle m$$

$$= \frac{8\pi^4 e^8 m_0}{h^5 c^2}\,\frac{1}{n^3 k^2}\,\mathrm{N}^3\triangle m \quad . \quad . \quad . \quad . \quad (29)$$

Writing $(\mathrm{Z} - s)$ for the effective nuclear charge, $\dfrac{2\pi^2 m_0 e^4}{h^3} = \mathrm{R}$

and $\left(\dfrac{2\pi e^2}{hc}\right)^2 = \alpha^2$

$$\triangle\nu_{\text{mag}} = \mathrm{R}\alpha^2\frac{(\mathrm{Z}-s)^3}{n^3}\,\frac{\triangle m}{k^2} \quad . \quad . \quad . \quad . \quad (30)$$

The relativity separation between two k, k' terms (21.2) is

$$\triangle\nu_{\text{rel}} = \mathrm{R}\alpha^2\frac{(\mathrm{Z}-s)^4}{n^3}\,\frac{k'-k}{kk'} \quad . \quad . \quad . \quad . \quad (31)$$

The magnetic calculation gives, noticeably, the same proportionality factor, $\mathrm{R}\alpha^2$, as the relativity calculation; but it indicates a variation of $\triangle\nu$ as the cube of the effective nuclear charge; and experiment indicates definitely, with close approximation, a fourth-power variation. Except for elements of very low atomic number, (30) gives separations much smaller than those observed. While, then, there may be a difference in magnetic energy of the terms, this only accounts, in general, for a small fraction of the total energy difference. There is, moreover, a further difficulty, for, according to (30), if the core had no magnetic moment, there would be no separations. The core of doublet atoms, however, has a zero moment, and yet there are the doublet separations. It is this difficulty which has given rise to the artificial character of much of theoretical treatment of the Zeeman effect. (As a simple instance, if Sommerfeld's j scheme is directly interpreted, the magnetic moment 1 of the silver atom in the normal s state is due to a contribution of 1 from the core, and 0 from the series electron.)

This aspect of the question has been emphasized by Pauli, who has advanced arguments against completed configurations (such as the doublet atom core) contributing towards the total angular momentum of the atom. He has also shown that the attribution of an anomalous $j : \mu$ ratio to the core only, leads to many difficulties.

It seems, then, undoubted that the customary magnetic interpretation of multiplet separations must be abandoned. A relativity type of formula must be adopted as an empirical representation of the facts; but the physical interpretation remains obscure. Before discussing this, Landé's derivation of his modified formula (22) will be outlined. If the series electron moved throughout its orbit under the influence of the charge Z_i (the mean effective charge when it is within the core) the separation would be given by (cf. 31)—

$$\triangle\nu_i = \mathrm{R}\alpha^2 \frac{Z_i^4}{n_i^3} \frac{k' - k}{kk'} \quad . \quad . \quad . \quad . \quad . \quad (32)$$

It is the inner part of the orbit on which the change of energy primarily depends; let t be the total time of describing the orbit, t_i the part within the core, and t_a that outside (under the influence of the charge Z_a). Since t_i is small, $t_a \fallingdotseq t$ and

$$\triangle\nu = \triangle\nu_i \frac{t_i}{t} = \triangle\nu_i \frac{t_i}{t_a} \quad . \quad . \quad . \quad . \quad . \quad (32.1)$$

The ratio of t_i to t_a will be approximately the same as that of the times of revolution of an electron under the influence of charges Z_i and Z_a. From V (20), therefore,

$$\frac{t_i}{t_a} = \frac{n_i^3 Z_a^2}{n_a^3 Z_i^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (32.2)$$

Substituting (32) and (32.2) in (32.1),

$$\triangle\nu = \mathrm{R}\alpha^2 \frac{Z_a^2 Z_i^2}{n_a^3} \left(\frac{k' - k}{kk'}\right) \quad . \quad . \quad . \quad . \quad (33)$$

which is in agreement with (22) for $k = k' - 1$; and, as has already been stated, this agrees with the observations either for the doublet np_2, np_1 separations, or the triplet np_2, np_0 separations, putting $k' = 2$, $k = 1$.

Although a relativity type of formula fits the observations, it seems highly improbable that the energy difference of two terms such as np_1 and np_2 can be due to a difference in the relativity change of mass; the two orbits have the same shape (k being the same), and the precessional motion due to the mass variation should be the same for both. It may be that orbital precession can only occur about a particular atomic axis, but such a view has no theoretical basis. An empirical substitution of inner for azimuthal quantum numbers in (31) or (33) might seem attractive, but this does not lead to values in agreement either with the absolute or relative intervals observed. Moreover, as will be seen from (21), or more readily from V (12.1), when the relativity change in mass is involved, the term with the larger k has the smaller ν value (the electron is less tightly bound); now among the j components of a k term, the one with the largest j usually has the smallest ν value (that is, the electron is most loosely bound in the highest j state—an np_2 sodium doublet electron, for example, being more loosely bound than an np_1), but "inverted" terms also occur, particularly in complicated spectra, in which the highest j state corresponds to the most firmly bound electron. Partially inverted terms have also been found. These facts point to the conclusion that the multiplet separations are really magnetic in origin, and that they are mainly due to the action of the localized fields in the atom core (which may be intense even when the core has no resultant moment) through which the series electron moves when it is near the nucleus and its velocity is greatest. The effect of these internal fields would vary with the orientation of the electron orbit; that intervals may be normal, inverted or partially inverted becomes readily intelligible. As yet the magnetic theory has not proved capable of yielding the correct formula, but the fact that the very crude assumptions on which (30) is based lead to a formula with the same proportionality constants as that which covers the observations supports the view that an adequate magnetic treatment may yet be given. This does not mean that the relativity theory is incorrect. The relativity correction must be applied to individual k terms, and separations such as that between L_I and L_{III} (corresponding to similarly orientated orbits with $nk = 21$ and 22) in the X-ray region, or between ns and np (when the orbits are similarly orientated) in the optical region, must still be regarded as relativity + screening separations. If this view is correct, the fact that the $L_{II} - L_{III}$, or $np_1 - np_2$ separations fit a relativity formula is fortuitous, involving, as it does, an incorrect assignment of azimuthal quantum numbers to the terms concerned.

Summarizing, it may be said that quantum magnetic theory enables a general qualitative interpretation to be given of multiplet structure and the Zeeman effect. The simpler phenomena can be explained on the basis of the usual quantum assumptions; in particular, individual electron orbits may be characterized by integral magneton numbers. For complex systems, independently of mathematical difficulties, the appropriate formulation of quantum conditions is far from being clear. (Of course, even should they be found, the inherent problem as to the significance of quantum conditions remains unsolved.) A great deal of experimental work has been done, but the need for much more is apparent. In some ways the experimental results are simpler than the theories. The theories as yet are halting and tentative. In spite of this, few fields seem more rich in promise of shedding light on the fundamental problems of the structure of the atom and the nature of radiation than that surveyed in the present chapter.

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This invaluable monograph deals both with the theoretical and experimental sides of the subject. It contains a beautiful series of reproductions of Zeeman pattern photographs. A bibliography is given of the more important papers between 1914 and the beginning of 1924. (For earlier references, see Zeeman : *Magneto-optics,* Macmillan, 1913.)

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Zeeman. "Magnetische Zerlegung der Spektrallinien," and
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Lorentz discusses very fully the problem of magnetic energy and its "localization." When attempts are made at a rigorous theoretical treatment of the effect of a magnetic field on an electronic system, whether from a purely classical or a quantum standpoint, many difficulties become prominent which it has only been possible to touch on in this book.

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Further references will be found in Chapter XIV.

CHAPTER XI

OTHER MAGNETO-OPTICAL EFFECTS

1. The Faraday and Kerr Effects. Magnetic Double Refraction

DURING the past few years the investigation of the Zeeman effect on line spectra has advanced with astonishing rapidity, and it has been considered at some length in the last chapter, partly for this reason, and partly because the results have so direct a bearing on the theory of atomic structure. Other magneto-optical phenomena have lain rather off the direct track of recent research, and they will not be treated here in detail, as admirable accounts of much of the work which has been done are to be found in standard books on Optics.

It will be sufficient to recall the salient characteristics of the more important phenomena. Their connection with the fundamental Zeeman effect will be briefly discussed, and also their significance from the point of view of the classical-quantum dilemmas; for magneto-optics provides some of the most interesting meeting-grounds for quantum and classical theories.

The rotation produced by transmission through a medium placed in a magnetic field of the plane of polarization of a beam of light travelling parallel to the lines of force was discovered by Faraday in 1845. The absolute direction of rotation is the same whether the light passes in the same direction as the field or the opposite. The magnitude of the effect, and its sign, have been measured for a large number of substances, solids, liquids and gases. The rotation is proportional to the field (Verdet) except in ferromagnetics, in which it is proportional to the intensity of magnetization (Kundt). (Kundt's rule will actually cover all cases, since the magnetic susceptibility is independent of the field except for ferromagnetics.) The majority of substances produce a positive rotation, that is a rotation in the same direction as the current producing the field, as is predicted by the Hall effect theory. The sign of the effect does not depend on whether the substance is dia- or para-magnetic, for while ferrous and ferric salts give a negative, cobalt and nickel salts give a positive rotation ; negative diamagnetics (e.g. titanium chloride) are, however, infrequent.

The rotation varies with the wave-length of the light, approximately inversely as the square over restricted ranges in which there are no absorption bands. The rotation for iron, nickel and cobalt, however, increases with wave-length in the visible region. Let R be the specific rotation (unit length, unit field) and n the refractive index. The magnetic rotatory dispersion may then generally be approximately represented by a formula of the type

$$R = \frac{1}{n}\left\{\frac{A}{\lambda^2} + \frac{B_m\lambda^2}{(\lambda^2 - \lambda_m{}^2)^2} + \ldots\right\} \quad . \quad . \quad . \quad (1)$$

λ_m being the wave-length corresponding to an absorption band. This formula indicates a rotation of the same sign on both sides of λ_m, increasing as λ approaches λ_m, as is almost invariably found, as for sodium vapour. There is some evidence for the occasional occurrence of "anomalous" rotatory dispersion, Elias having found a decrease on rotation on approach to an absorption band from the short wave-length side with a salt of praseodymium ; this, however, is probably due to secondary effects of a kind indicated by Voigt's theory (see below).

The phenomena accompanying the reflection of light from a surface of a magnetized ferromagnetic, some types of which were first observed by Kerr (1871), are rather complicated. The simplest effect is a rotation of the plane of polarization accompanying normal reflection for magnetization normal to the surface. This is not accounted for by the Faraday rotation due to partial penetration, being in the opposite sense. In general (oblique incidence, and oblique magnetization) plane-polarized is converted into elliptically polarized light, this effect being superposed on the rotation. Surface films have a marked influence. Voigt has worked out a theory, formally satisfactory, by taking into account the Faraday rotation and applying the appropriate electromagnetic boundary conditions for metallic surfaces. It is necessary to assume the existence of internal fields, and calculation leads to a value for these of the same order (10^7 gauss) as that postulated by Weiss.

In developing a theory of the Faraday effect the starting-point is to regard the plane-polarized light as split up into two components with opposite circular polarization. The rotation of the plane of polarization observed will depend on the difference in the refractive indices for the two components. This mode of attack is justified by the work of Brace, who succeeded in effecting the resolution of the components experimentally. Drude works out two theories, based on two different sets of assumptions. In the first "molecular currents" are assumed, and the centres of the corresponding electronic orbits are supposed to be set in vibration by the light waves. The assumptions lead to unsatisfactory results. The second theory is based on the Hall effect. It is supposed that quasi-elastically bound electrons are set in vibration by the light waves, and that they are then subject to a force arising from the magnetic field, at right angles to the field, and their velocity, and equal to $\frac{ev\mathrm{H}}{c}$. Essentially the field modifies the frequency of the forced circular vibrations set up by the light waves. Drude's expressions may be readily arrived at by making use of the fact that the modification in the frequency will simply be that due to the Larmor precession.

On the basis of the usual electron theory of dispersion, the refractive index, n, is given by

$$n^2 = 1 + \Sigma \frac{\mathrm{N}_m \frac{4\pi e^2}{m p_m^{\,2}}}{1 - \frac{p^2}{p_m^{\,2}}} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

where $p = 2\pi\nu = 2\pi\frac{c}{\lambda}$. ν_m is the natural frequency, corresponding to an absorption line, of the set of electrons of which there are N_m per unit volume. (2) only applies to regions sufficiently removed from ν_m that absorption can be neglected. Let n'', n' be the refractive indices for the two circular components with unit field; the specific rotation will then be given by

$$\mathrm{R} = \frac{\pi}{\lambda}(n'' - n') = \frac{2\pi}{\lambda}\delta n \quad . \quad . \quad . \quad . \quad . \qquad (3.1)$$

where $\delta n = n'' - n = n - n'$.

Now δn will depend simply on the change of frequency of the forced vibrations; remembering that δn applies to unit field, and neglecting second-order terms,

$$\delta n = \frac{dn}{d\mathrm{H}} = \frac{dn}{dp} \cdot \frac{dp}{d\mathrm{H}} \quad . \quad . \quad . \quad . \quad . \qquad (3.2)$$

From IV (8)

$$\mathrm{H}\frac{dp}{d\mathrm{H}} = o = -\frac{e\mathrm{H}}{2mc} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3.3)$$

Therefore $$\delta n = -\frac{e}{2mc}\frac{dn}{dp}$$

$$R = -\frac{\pi e}{mc\lambda}\cdot\frac{dn}{dp} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.4)$$

or, since $$dp = -2\pi c\lambda^{-2}d\lambda$$

$$R = \frac{e}{2mc^2}\lambda\frac{dn}{d\lambda} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.5)$$

Substituting from (2) in (3.4)—

$$R = -\frac{\pi}{2ne\lambda^2}\Sigma N_m\left(\frac{\frac{4\pi e^2}{mp_m^2}}{1-\frac{p^2}{p_m^2}}\right)^2 \quad . \quad . \quad . \quad . \quad (4)$$

This is equivalent to the result obtained by Drude. If there is one set of electrons with a high natural frequency ($p_m \gg p$), and one with a frequency corresponding to a wave-length λ_m, (4) may be expressed in the form of (1), in which

$$B_m = -N_m\frac{e^3\lambda_m^4}{2\pi m^2c^4} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.1)$$

The rotary dispersion of sodium vapour, even quite close to the D lines, is well expressed by

$$R = \frac{C\lambda^2}{(\lambda^2-\lambda_m^2)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.2)$$

If electrons alone are effective in producing the rotation, the Hall effect theory leads to the conclusion that the rotation should be positive, increasing to a maximum on either side of an absorption band. It leads to formulæ which cover the experiments on a number of substances over wide ranges of wave-lengths, and is of interest as being a quite straightforward and natural development of the classical electron theory of dispersion. Just because of this, however, it is open to serious criticism, for it is impossible to accept as satisfactory a theory which involves an interaction between matter and radiation of quite a different character from that which more direct experiments have indicated. Independently of this, however, it is inadequate, for although rotations associated with lines due to atomic spectra may be positive, negative rotations are also found, not only in association with absorption bands and lines of solids, but also with lines in the absorption spectra of gases. This is shown in particular by the beautiful work of Wood on the rotations associated with lines in the channelled absorption spectrum of sodium vapour.

The theories of Voigt are formal; but they are more satisfactory, for the magneto-rotation phenomena are linked up directly with the Zeeman effect. Consider an atomic gas which gives rise to an emission line showing the normal Zeeman effect. In a field, longitudinally, the absorption spectrum will show two lines, corresponding to the absorption of light circularly polarized in opposite directions (the longitudinal inverse Zeeman effect). If the natural single absorption line is associated with dispersion (having a frequency corresponding to $p_m/2\pi$ in equation 2), the dispersion curve will split up into two, when the line doubles in the field, corresponding to different refractive indices for light circularly polarized in opposite directions. The rotation will depend on the difference in the two refractive indices (3.1); on either side of the absorption doublet the rotation will be positive, and in between the components negative. This is illustrated diagrammatically by the curves of Fig. 44, in which the distance between the absorption lines is greatly exaggerated.

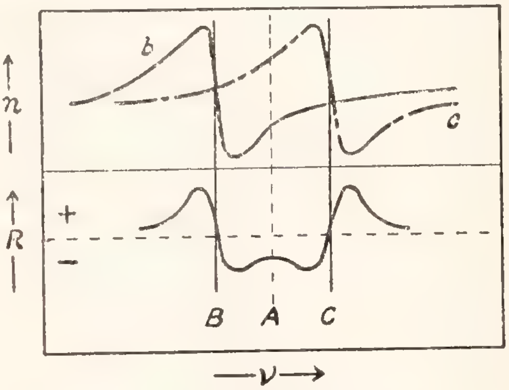

FIG. 44.—Dispersion and Magnetic Rotation Curves.

A, position of undisplaced absorption line. B, C, absorption lines; *b*, *c*, dispersion curves, for oppositely circularly polarized light with a magnetic field.

Curves of precisely this form have been found experimentally by Zeeman for sodium vapour.

The Zeeman-effect treatment enabled Voigt to predict that transversely to the field magnetic double refraction should occur. Just as the longitudinal splitting of the absorption line results in oppositely circularly polarized rays travelling with different velocities, the transverse splitting results in different velocities for plane-polarized (⊥ and ∥) components of the light, and so in double refraction. The theoretical and experimental curves again agree well (Voigt and Wiechert, and Zeeman and Geest). It should be noted, however, that some liquids, such as nitro-benzol, investigated by Cotton and Mouton, show much greater magnetic double refraction than would be anticipated from the magnetic rotation. It seems probable that there must be some mechanism involved, of the nature of molecular orientation, other than that in the Zeeman effect.

The Zeeman effect on band spectra lines has been studied notably by Dufour, Fortrat and Deslandres; and on the absorption lines of rare-earth salt crystals by Becquerel, du Bois and Elias. It is noteworthy that the effect is much more varied than for atomic spectrum lines. On longitudinal observation, for some lines there is no effect, and for others there is displacement with polarization in the opposite sense to that usually observed. As this cannot be attributed to positive electrons, it must be due to internal molecular or crystalline reverse fields. Although the Zeeman effect on band spectra has as yet been little investigated—natural band spectra are only beginning to be co-ordinated—the anomalous negative magnetic rotations observed are undoubtedly to be connected with the anomalous Zeeman effects.

Phenomena associated with spectra other than atomic line spectra provide an unlimited and practically unexplored region for research, whose richness is indicated by the finds that have already been made. Discussion at present would hardly be profitable. A few points connected with line spectra effects may, however, be considered.

From a quantum point of view the absorption of light of frequency corresponding to a magnetic component of a spectral line involves a transition of the atom between two definite energy states in each of which the atom has a definite orientation relative to an applied magnetic field. In absorption, the initial state is one of the possible normal states of the atom. The inverse Zeeman effect indicates that absorption of a definite component only occurs if the light has not only the appropriate frequency, but also the appropriate polarization. Magnetic rotation, however, and indeed dispersion phenomena generally, show that there is some interaction between radiation and matter even when the frequency of the light is different from that corresponding to quantum transitions between a normal and a higher state, and that this interaction is more pronounced the more closely the two frequencies agree. Line absorption and "resonance" may be regarded as quantum effects. They are associated with the complicated dispersion phenomena in the immediate neighbourhood of an absorption line. Resonance is, however, simply a special case of scattering, with the associated normal dispersion, so that there is no abrupt transition from a region in which classical scattering and dispersion occur, to one characterized by quantum phenomena. Scattering may be regarded as quantum absorption (with a transition to a "non-stationary" state) with "immediate" re-emission; though this view has not yet been developed in any satisfactory manner quantitatively, there are indications that it may not be unfruitful.

The essential importance of magneto-optics lies in the fact that the effects studied are connected with individual components of spectral lines, due to quantum transitions between two single sharply defined stationary states.

The quantum interpretation of the Zeeman effect which is gradually becoming more coherent provides a guide in other magneto-optical investigations; and these in turn will undoubtedly throw much light on optical phenomena generally, which are at present capable of only vague descriptive explanation by an arbitrary mixture of two mutually incompatible theories.

2. The Influence of a Magnetic Field on the Polarization of Resonance Radiation

When sodium vapour is illuminated by sodium light, the D lines are re-emitted as resonance radiation. On the one hand, as has been pointed out, resonance may be regarded classically as enhanced scattering, occurring when the frequency of the incident light is equal to the natural frequency of the quasi-elastically bound electrons; on the other, it may be regarded as a special case of fluorescence, and as such can be most readily explained on a quantum-theory basis. Absorption of D light involves a transition of the sodium atom from the normal s to a p state. If the density of the vapour is considerable, the excited atoms may undergo collisions of the "second kind" resulting in a $p \rightarrow s$ transition without radiation, the energy being transformed into kinetic energy of the colliding atom or molecule. If, however, the vapour pressure is small, so that the average life of the excited atom (of the order of 10^{-8} sec.) is short compared with the time between collisions, the energy absorbed will be re-emitted as resonance radiation resulting from the transition. While scattered radiation shows peculiarities as to distribution and polarization, fluorescent or resonance radiation is generally unpolarized and emitted equally in all directions—as, indeed, would be anticipated, if definite absorption and re-emission are involved. Even with gases, however, fluorescent radiation was sometimes found to be polarized; but the polarization phenomena seemed very erratic, and different investigators obtained most divergent results. This is probably to be traced to the marked effect which may be produced by even very small magnetic fields—so that the results might depend on the number of iron stands included in the apparatus, and whether the tubes were placed east and west or north and south ! Some recent experiments of Wood and Ellett have cleared up many of the anomalies, and are of the utmost importance for magneto-optical theory.

Experiments were carried out with sodium vapour excited by the D lines (5,896, 5,890 p_1, $p_2 \longrightarrow s$), and with mercury vapour excited by the mercury resonance line $\lambda = 2{,}537$ ($p_1 \longrightarrow S$). The sodium results will be considered first. The sodium vapour, at a temperature of 150–200°, was contained in a suitable bulb, and illuminated by a beam of light, whose polarization was under control, travelling in the Y direction (Fig. 45).

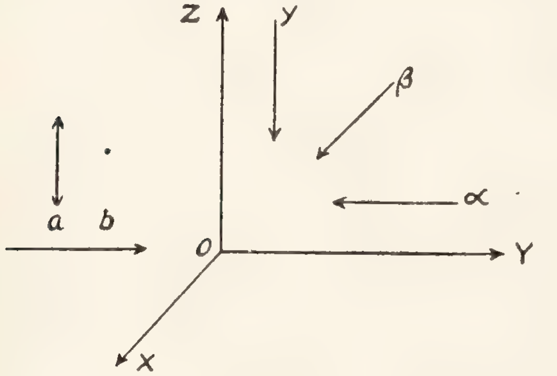

FIG. 45.

OY, direction of incident light. OX, direction of observation. α, β, γ, magnetic field. a, b, electric vector of incident light.

The resonance radiation was observed along OX ; a magnetic field could be applied in any desired direction. The earth's field was first compensated. It will be convenient to define the state of polarization by the direction of the electric vector E for the exciting, and R for the resonance radiation. If J_1 and J_2 are the intensities of two components of the radiation, plane-polarized at right angles, then the degree of polarization, δ, may be defined by

$$\delta = \frac{J_1 - J_2}{J_1 + J_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

In the absence of a field, with E ‖ Z, 5 per cent. polarization was observed. This could be practically destroyed by the application of a field of 100 gauss parallel to OX (that is, parallel to the direction of observation, and to the direction of the magnetic vector of the incident light). The effects were observed with E | OZ, and E ‖ OX.

E ‖ OZ.—By applying a magnetic field along OY (α, Fig. 45) the polarization could be increased to 30 per cent. (R ‖ OZ). As H was rotated in the plane ZOY from α to β, the plane of polarization rotated with it (R remaining ⊥ H) but the degree of polarization decreased to zero. On continuing the rotation of H from β to γ, the degree of polarization increased, but the plane of polarization rotated in the opposite direction until, with H ॥ OZ, strong polarization was again obtained with R parallel to OZ. Some experiments by Ellett, and by Hanle, have shown that the angle which H makes with OY for zero polarization is not 45°, as was at first supposed, but that it lies between 30° and 40°.

E ॥ OX.—With H ॥ OY (α) 20–30 per cent. polarization was obtained with R ॥ OZ. Rotation of H from α to γ was accompanied by rotation of the plane of polarization, the degree remaining unaltered, so that H ॥ OZ (γ) gave R ॥ OY.

The destruction of the initial polarization (with E ॥ OZ) by a field H ॥ OX, as observed in the OX direction, was found to be accompanied by the appearance of plane polarization along OY (R ॥ OZ) and along OZ (R ॥ OY).

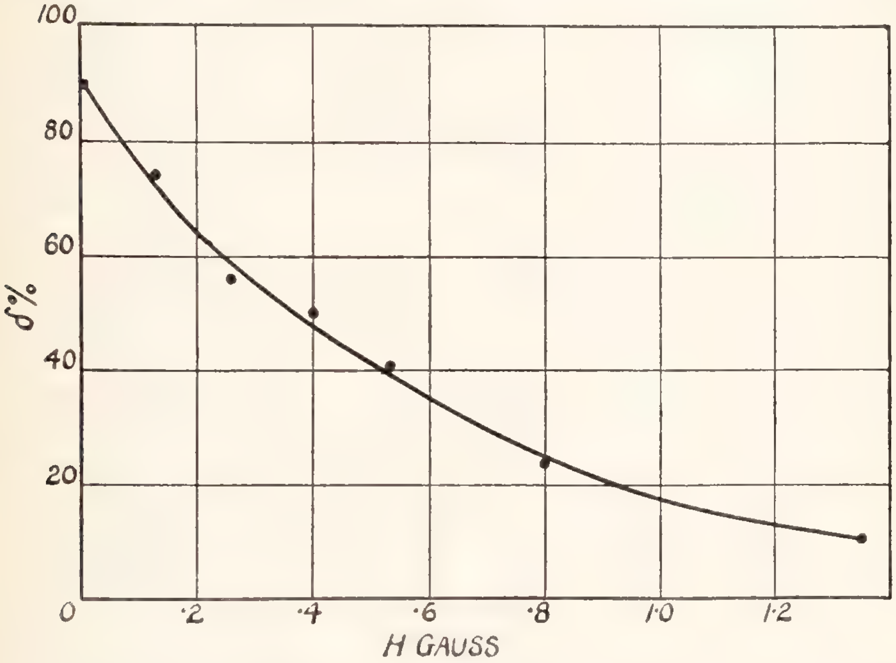

FIG. 46.—Effect of a Field on the Polarization of Mercury Vapour Resonance Radiation.
E ॥ OZ. H ॥ OX.

With mercury the experiments were more difficult owing to the necessity of employing purely photographic methods. In the absence of a field, with E ॥ OZ, 90 per cent. polarization was observed, and this was practically destroyed by a field of 1·4 gauss, with H ॥ OX (see Fig. 46).

With E ॥ OX, the polarization was very feeble, but became strong on the application of fields of the order of 1 gauss in the ZOY plane.

A general qualitative explanation, due to Darwin, of some of the results was given in Wood and Ellett's paper ; the experiments were subsequently considered more precisely, on the basis of the Zeeman effect, by Joos, Breit, Pringsheim and others, with agreement as to essential particulars.

The magnetic levels involved in the D-line transitions are shown in Fig. 47 (cf. Table XXVI), with the relative intensities of the lines as observed in the transverse Zeeman effect.

In Wood's experiments the separate components were not resolved, but the resultant polarization observed will depend on the relative intensities of the components present. Let n_1, n_2 . . . be the equilibrium numbers of atoms in the states 1, 2 . . . , k_a, k_b . . . the probabilities of absorption transitions, l_a, l_b . . . the probabilities of emission transitions. For equilibrium the number of transitions to any particular state in a given time must be equal to the number from it.

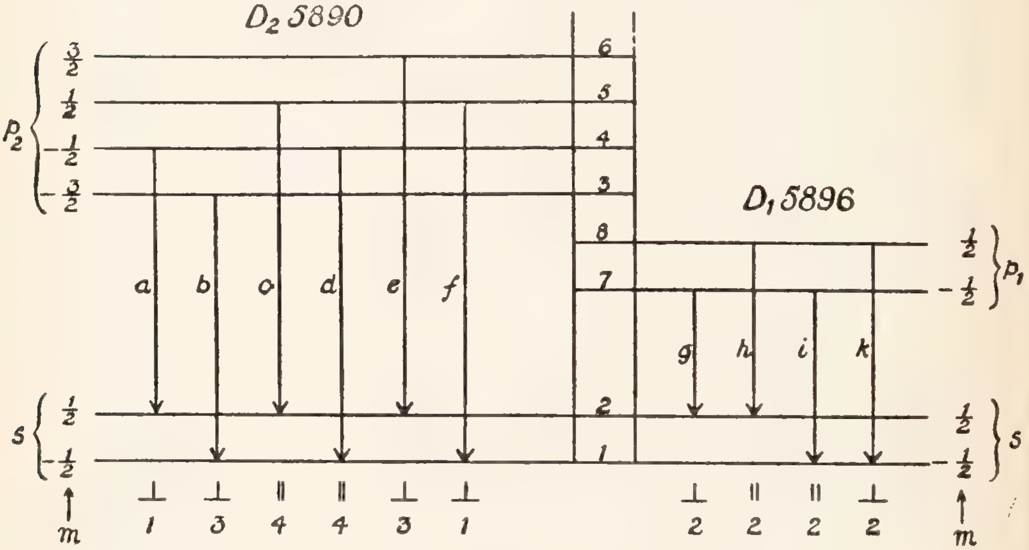

FIG. 47.—D-line Transitions.

For the state 4—

$$(l_a + l_d)n_4 = k_a n_1 + k_d n_2 \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

with similar equations for the other states.

From the Gerlach and Stern experiments $n_1 \fallingdotseq n_2$; as only relative numbers are required, this number may be taken as the unit ; for convenience, writing a, b . . . for the relative numbers of the corresponding emission transitions, (6) may be written

$$a + d = k_a + k_d \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6.1)$$

The complete set of equilibrium equations is then

$$\left.\begin{array}{rlrl} a+d &= k_a+k_d & & \\ b &= k_b & g+i &= k_g+k_i \\ c+f &= k_c+k_f & h+k &= k_h+k_k \\ e &= k_e & & \end{array}\right\} \quad . \quad . \quad (7)$$

The relative number of transitions a, b, c . . . under ordinary excitation conditions can be derived from the observed relative intensities of the lines in the Zeeman effect. These intensities, as deduced from the polarization and summation rules (Ch. X, sect. 5), are given in Fig. 47, and, considered as "ideal" numbers, are in good agreement with experiment. Since on transverse observation the observed ratio of the $\perp$ to the $\parallel$ components is only half the corresponding total intensity ratio, the following ratios for relative numbers of transitions from given levels may be deduced—

$$\left.\begin{array}{rlrl} a:d &= 1:2 & g:i &= 2:1 \\ c:f &= 2:1 & h:k &= 1:2 \end{array}\right\} \quad . \quad . \quad . \quad (8)$$

If the atoms are excited by unpolarized light, in the absence of a field, all the absorption transitions can occur; but polarization of the incident light and the presence of fields may impose restrictions on the possible absorption transitions; there may be no transitions to some of the p levels, with the result that certain components may be absent from the emitted light. Thus Foote, Ruark and Mohler observed that D_2 resonance radiation excited by polarized incident light (in Fig. 45, with E $\parallel$ OZ, H $\parallel$ OZ, observation along OX) showed only four magnetic components (a, c, d, f in Fig. 47) instead of the usual six.

The Wood and Ellett experiments may now be considered, the cases being represented, with reference to Fig. 45, as $a\alpha$, β, γ and $b\alpha$, β, γ. It should be noted that the plane-polarized incident radiation may be regarded as made up of two circularly polarized components. With a magnetic field along OY, in the ordinary Zeeman effect, only circularly polarized ($\perp$) components, corresponding to transitions for which $\triangle m = \pm 1$, are emitted along OY; correspondingly, only such components will be absorbed. Absorption transitions for which $\triangle m = 0$ will not occur. For case $a\alpha$, k_c, k_d, k_h, k_i may be put equal to 0, and equations (7) become—

$$\left.\begin{array}{rlrl} a+d &= 1+0 & & \\ b &= 3 & g+i &= 2+0 \\ c+f &= 0+1 & h+k &= 0+2 \\ e &= 3 & & \end{array}\right\} \quad . \quad . \quad (7.1)$$

From (7.1), making use of (8), the relative numbers of emission transitions are readily deduced ; these will give $\perp$ or $\parallel$ components according as $\triangle m = \pm 1$, or 0.

The relative numbers of transitions, obtained by multiplying the numbers directly given by (7.1) and (8) by 3 to give integers, are as follows :—

D_2		D_1	
$\perp$	$\parallel$	$\perp$	$\parallel$
a 1			
b 9	c 2	g 4	h 2
e 9	d 2	k 4	i 2
f 1			

Remembering that the relative intensity of $\parallel$ to $\perp$ components observed is double that of the number of actual transitions, it will be seen from (5) that the D_1 resonance radiation will be unpolarized, and the D_2 polarized with $\delta = \dfrac{20 - 8}{28} = 43$ per cent.

Writing $J_\perp$ and $J_\parallel$ for the total resultant intensities of the components polarized with the electric vector perpendicular and parallel to H, for case *aa*—

$$J_\perp = 28 \qquad J_\parallel = 16$$

$$\delta = \frac{28 - 16}{44} = 27 \text{ per cent.}$$

The total resultant effect will be a polarization, such that $\delta = 27$ per cent., and with the electric vector perpendicular to H (or $R \parallel OZ$).

In case *aγ* the only light present in the incident radiation which can be absorbed is that corresponding to the $\parallel$ components which would be emitted. The only absorption transitions which can occur are those for which $\triangle m = 0$; $k_c = k_d = 4$; $k_h = k_i = 2$; the rest of the k's become zero. Proceeding as in case *aa*, there results

$$J_\perp = 16 \qquad J_\parallel = 40$$

$$\delta = 43 \text{ per cent.}$$

The resonance radiation will be strongly polarized with $R \parallel OZ$.

When H is inclined at an angle θ with OY, the incident radiation may be resolved into components with E perpendicular and parallel to H (corresponding to *aa* and *aγ*) with intensities respectively proportional to $\cos^2 \theta$ and $\sin^2 \theta$. For the relative intensities of the $\perp$ and $\parallel$ components

$$J_\perp = 28 \cos^2 \theta + 16 \sin^2 \theta.$$

$$J_\parallel = 16 \cos^2 \theta + 40 \sin^2 \theta.$$

This gives for the total intensity

$$J = k(1 + \tfrac{3}{11} \sin^2 \theta) \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and for the polarization

$$\delta = \frac{3(\cos^2 \theta - 2 \sin^2 \theta)}{11(1 + \frac{3}{11} \sin^2 \theta)} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

the resultant electric vector R being ⊥ or ∥ to H according as δ is positive or negative. The general expression (10) covers the cases *aa* ($\theta = 0°$) and *aγ* ($\theta = 90°$) already considered, and it further shows that δ should be zero for $\theta = \tan^{-1}\left(\frac{1}{\sqrt{2}}\right) = 35° \, 16'$.

With the electric vector of the incident light parallel to OX, the conditions are the same as in case *aa*, whatever the direction of H in the plane ZOY. The degree of polarization will therefore be 27 per cent., with R ⊥ H.

The agreement with experiment is on the whole quite good. The treatment given above is essentially similar to that of Joos and Breit, though differing in points of detail. Joos does not take into account the difference in the ratio of the number of transitions to observed intensity for ⊥ and ∥ components; while Breit makes use of the rough experimental values for the intensities.

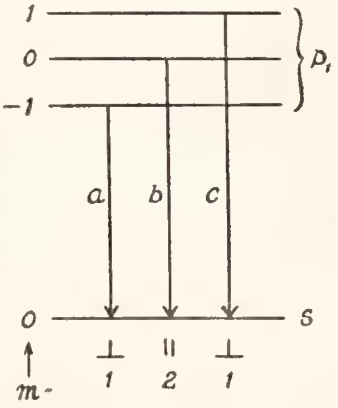

FIG. 48.—Transitions for Hg λ = 2,537.

When there is no field, it is necessary to average the results obtained for fields in any direction. Doing this, Breit deduces a 5·5 per cent. polarization for sodium with no field, with polarized exciting radiation—in close agreement with the value observed by Wood.

The resonance radiation transition diagram for mercury is shown in Fig. 48.

With the magnetic field in the plane ZOY, making an angle θ with OY (the incident beam direction) and with the electric vector perpendicular to the direction of observation (E ∥ OZ),

$$\delta = \frac{\cos^2 \theta - 2 \sin^2 \theta}{\cos^2 \theta + 2 \sin^2 \theta}$$

$$J \propto C(1 + \sin^2 \theta) \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

giving $\delta = +1$ and -1 (complete polarization) for $\theta = 0$ and $90°$, and $\delta = 0$ for $\theta = 35° \; 16'$.

With the exciting vector in the direction of observation ($E \parallel OX$)—

$$\delta = 1 \qquad\qquad J = C \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

With the incident light unpolarized

$$\delta = \frac{\cos^2 \theta - \sin^2 \theta}{\cos^2 \theta + \sin^2 \theta} \quad . \quad . \quad . \quad . \quad . \qquad (13)$$

giving again complete polarization for $H \mid OZ$ or $H \parallel OY$ but zero polarization for $\theta = 45°$.

In the absence of a field, with the atoms orientated at random, not more than 50 per cent. polarization would be expected; and the fact that 90 per cent. polarization was actually observed (Fig. 46) constitutes one of the most surprising results of the Wood and Ellett experiments. It suggests that orientation of the atoms must occur in the field of the light rays; it would be premature to speculate on this until more experiments have been carried out.

Breit and Pringsheim have considered the strength of the field required to destroy the initial polarization; this has been tentatively brought into connection with the period of the corresponding Larmor precession, given by

$$\tau = \frac{2\pi}{o} = \frac{4\pi mc}{eH} = \frac{7{\cdot}1 \times 10^{-7}}{H} \quad . \quad . \quad . \qquad (14)$$

It may be supposed that if τ is small compared with the time between collisions, spatial orientation, as determined by the field, may establish itself. That fields of 1 or 2 gauss with mercury were comparable in their effect with fields of 100 gauss for sodium is possibly to be attributed to the greater disturbance due to neighbouring atoms in sodium; the temperature of the sodium vapour being considerably greater than that of the mercury. This view is supported by some experiments of Gerlach and Schütz, who found that magnetic rotation in the absorption spectrum of sodium vapour occurred for fields of a few tenths of a gauss at a pressure of 1×10^{-3} mm., but that at 7×10^{-3} mm. no effect was produced by a field of 1·2 gauss.

Some recent experiments of Hanle on mercury vapour should be mentioned. He examined the influence of small fields applied along OY (Fig. 45) on the natural plane-polarized resonance radiation, observing as nearly as possible in the OY direction. If the fields are small, their effect is to produce simply a rotation of the plane of polarization, and from the magnitude of this, interpreted according to quantum ideas, an estimate of the mean life of the excited atoms may be obtained. Hanle also carried out experiments with elliptically polarized light.

While the polarization of the mercury vapour resonance radiation is practically completely destroyed by steady fields of 1·4 gauss, Breit and Ellett have found that the influence of an alternating field is negligible if the frequency exceeds 10^7 per second, but quite pronounced at a frequency of 5×10^6 per second. This may give an indication of the mean life period of an excited atom, or of the rapidity with which the "quantization" of an atom responds to the effect of a magnetic field. It may be noted that the critical frequency is of the same order as the corresponding Larmor frequency.

Investigations such as those reviewed in this section are as yet in their infancy, and while further discussion would be at present somewhat out of proportion, there can be little doubt of the power of the methods for attacking fundamental problems as to the nature of radiation and its interaction with matter.

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BREIT and ELLETT. "The depolarising influence of a rapidly changing magnetic field on the resonance radiation," *Phys. Rev.*, 25, 888 (1925). (2)

The following paper is of considerable cognate interest in connection with the mercury resonance experiments—

FÜCHTBAUER, JOOS und DINKELACKER. "Über Intensität, Verbreiterung und Druckverschiebung von Spektrallinien, insbesondere der Absorptionslinie 2537 des Quecksilbers," *Ann. der Phys.* 71, 204 (1923).

CHAPTER XII

DIAMAGNETISM

1. General. Pascal's Work

WHILE paramagnetism is a particular property of electronic systems possessing unbalanced electronic orbits capable of changing their orientations, diamagnetism is common to all matter. Like the Zeeman effect, it results from the Larmor precession due to the application of a magnetic field. For an atom, consisting of electrons rotating about a single centre of force, as has been shown in the discussion of Langevin's theory (IV, 9) the atomic diamagnetic susceptibility is given by

$$\chi_{At} = -\frac{e^2}{4mc^2}\sum_n \overline{r^2} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

the summation being extended over the n electrons in the atom, and $\overline{r^2}$ being the mean square of the radius of the projected orbit in a plane perpendicular to the field. If r_1 (components x_1, y_1, z_1) is the distance of an electron from the nucleus, then for an atom symmetrical in the sense that $\overline{x_1{}^2} = \overline{y_1{}^2} = \overline{z_1{}^2}$,

$$\Sigma\overline{r^2} = \tfrac{2}{3}\Sigma\overline{r_1{}^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1.1)$$

and the mean square radius of all the electronic orbits in the atom will be given by

$$\overline{r_1{}^2} = -\frac{6mc^2}{ne^2}\chi_{At} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1.2)$$

In molecules, the orbits of the inner electrons of the constituent atoms will be little changed. The outer "shared" electrons, however, will have their orbits distorted; moreover, they will be moving under the influence of more than one centre of force, and the Larmor theorem can no longer be applied in its simple form. Atomic (or ionic) diamagnetism should be an additive property as long as the atoms (or ions) maintain their individuality; but when they definitely combine into a more complex system, constitutive effects may make an appearance.

The influence of chemical combination on magnetic properties was studied by Pascal in a very extensive series of magneto-chemical investigations (1908–13). From his own measurements and those of Curie, Pascal concluded that the diamagnetic susceptibility of "metalloids" could be represented by an expression of the form

$$\chi_A = -10^{-7}e^{\alpha + \beta A} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where A is the atomic weight, and α and β constants for each family. For P, Sb, Bi, $\alpha = 2{\cdot}058$, $\beta = {\cdot}00418$; for Cl, Br, I, $\alpha = 2{\cdot}195$, $\beta = {\cdot}00380$; and for S, Se, Te, $\alpha = 2{\cdot}281$, $\beta = {\cdot}00505$. Pascal's own measurements were mainly made on liquids, by a fairly simple form of U-tube method. The volume susceptibilities of a number of gases were deduced from his measurements on them as liquids; the values obtained (reduced to 0° C., 760 mm.) and also the gram-molecular susceptibilities are shown in the following table:

	$-\kappa \times 10^{10}$.	$-\chi_M \times 10^6$.
SO_2	8·5	19·0
NH_3	8·5	19·0
C_2N_2	10·1	22·5
N_2O_3	10·3	23·0
N_2O_4	11·3	25·2
CH_3NH_2	12·5	28·0
CH_3Cl	15·1	33·5
Cl_2	18·7	41·5

TABLE XXXI.—Susceptibilities of Gases (Pascal).

For all except the last two gases, Pascal noted that the susceptibility was roughly a function of the number of atoms, n, the molecule contained, being given by

$$\kappa = -1{\cdot}04\,(5 + n)\,10^{-10}.$$

This relation, being neither accurate nor general, seems, however, to have no particular significance.

More recent measurements on normal paramagnetic solutions, already considered, have superseded those of Pascal; his observations on some complex salt solutions have considerable interest and will be discussed later (Ch. XV). It became clear that an ion changes its magnetic properties when it enters into an ion complex; and that magnetic properties in general were characteristic not so much of the individual atom, as of the group or radicle to which the atom belonged.

The most significant conclusions, from the point of view of the theory of diamagnetism, were drawn from the study of organic liquids. For these Pascal found that the molecular susceptibility could be expressed by

$$\chi_M = \Sigma a \chi_A + \lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where a is the number of atoms of susceptibility χ_A, and λ is a constitutive constant depending on the nature of the linkages between the atoms. Pascal's procedure may be illustrated by a few simple examples. It was found that the differences in the susceptibilities of mono-halogen benzene derivatives were those which would be anticipated, on the basis of an additive law, from the directly determined susceptibilities of the halogens themselves. The change due to the replacement of a hydrogen by a chlorine atom then enabled the atomic susceptibility constant for H to be found; the constant for the CH_2 group was determined by the differences in the susceptibilities of members of the aliphatic C_nH_{2n} series, and the constant for the C atom could then be found. In this way were deduced

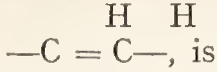
$$\chi_{CH_2} = -12{\cdot}3 \times 10^{-6} \qquad \chi_H = 3{\cdot}05 \times 10^{-6} \qquad \chi_C = 6{\cdot}2 \times 10^{-6}$$

The value of χ_C agreed very closely with that found directly for sugar carbon. That the addition of a CH_2 group increased the molecular susceptibility by a constant amount was verified by measurements on compounds of many types—alcohols, aldehydes, ketones, acids and aliphatic and aromatic amines. The values deduced for ionic constants in a similar manner have been given in Table VII (Ch. VI). To these the following values (corrected, with $\chi = 7{\cdot}2 \times 10^{-6}$ for water, in place of $7{\cdot}5 \times 10^{-6}$) for atoms in combination, may be added.

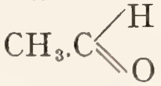
	$-\chi_A \times 10^6$.
H	2·95
C	6·0
N	5·6
O	4·6
P	26·6
S	15·1

TABLE XXXII.—Atomic Susceptibility Constants (Pascal).

It will be noticed that though the oxygen molecule is paramagnetic, the oxygen atom, in combination, has a diamagnetic effect.

In general, the molecular diamagnetic susceptibility is not simply equal to the sum of the susceptibilities of the atoms; but valency links of a definite type exert the same effect in different compounds. Thus, for the ethylenic link $\lambda = + 5{\cdot}5 \times 10^{-6}$ (see equation 3), and the susceptibility of C_nH_{2n}, containing one group  $\overset{H}{-C} = \overset{H}{C}-$, is given by

$$\chi_M = (- 6{\cdot}0n - 2 \times 2{\cdot}95n + 5{\cdot}5) \times 10^{-6}$$

For the benzene and naphthalene groups $\lambda = - 1{\cdot}5 \times 10^{-6}$ and $- 6{\cdot}1 \times 10^{-6}$ respectively. Oxygen exerts a different effect, according as it is linked with two different atoms, as in CH_3OH (when, as in Table XXXII, $\chi_0 = - 4{\cdot}6 \times 10^{-6}$), or doubly linked to a carbon atom, as in  $CH_3.C{<}^{H}_{O}$ (when $\chi_0 = + 1{\cdot}8 \times 10^{-6}$).

It seems as if some light might be shed on the electronic significance of valency bonds by a consideration of the constitutive constants deduced by Pascal, a question which will be briefly discussed later (Ch. XV).

The essential point which emerges from Pascal's work is that diamagnetic atoms combine to give diamagnetic molecules, and that to a first approximation the effects are additive. This behaviour contrasts markedly with that of paramagnetic atoms which frequently lose their paramagnetic character on combination.

The actual magnitude of the diamagnetic constants are in agreement with theoretical expectations. From (1.2) with n as the number of electrons in the atom, and N Avogadro's constant,

$$\overline{r_1^2} = - \frac{6mc^2}{Nne^2}\chi_A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

$$\overline{r_1^2} = - \left[\frac{\cdot351}{n}(\chi_A \times 10^6)\right] \times 10^{-16} \quad . \quad . \quad . \qquad (4.1)$$

As will be readily seen from Table XXXII, this gives values for $\sqrt{\overline{r_1^2}}$ for H, C, N . . . of $1{\cdot}1$, $\cdot59$, $\cdot53$ . . . A.U.—of the same order as those deduced from other evidence.

2. Diamagnetic Elements

The methods used by Honda and Owen in investigating the susceptibilities of elements have been briefly described in Chapter VI. Their results for diamagnetics are given in Table XXXIII, which is complementary to Table XIV for paramagnetics. D and I indicate a susceptibility numerically decreasing and increasing with temperature, C a constant susceptibility. Where there is an asterisk, the interpretation of the results is doubtful owing to the presence of iron. The susceptibilities given are those at room temperature. These,

		$-\chi \times 10^6$.	$-\chi_{At} \times 10^6$.	Variation with Temperature.	
4	Be	1·0	9·0	I*	
5	B	·7	7·6	I	170–400
				C	400–1,200
6	C	·49	6·0	C	−170–200
				I	200–1,200
14	Si	·13	3·8	C	
15	P	·90	27·9	C	
16	S	·49	16·0	C	
29	Cu	·085	5·4	D	
30	Zn	·155	10·2	C	−170–300
				D	300–700
31	Ga	·24	16·8	D*	−170–30
32	Ge	·12	8·7	D	−170–900
33	As	·31	25·3	C*	
34	Se	·32	25·4	C	
35	Br	·40	32·0	C	−170–18
38	Sr	·2 ?	17·5		
40	Zr	·45	40·9	D*	500–1,200
47	Ag	·20	21·6	I*	
48	Cd	·18	20·2	C	−170–300
				D*	300–700
49	In	·11	12·6	D*	−170–150
50	Sn	·35	41·5		
51	Sb	·82	99·5	C	−170–50
				D	50–631
52	Te	·32	40·5	D	
53	I	·36	45·7	I	−170–114
				D	114–200
55	Cs	·10	13·3	C	
79	Au	·15	29·6	C	
80	Hg	·19	38·1	I	−170– −39
				C	−39–350
81	Tl	·24	49·1	D	
82	Pb	·12	24·8	D	−170–327
				C	327–600
83	Bi	1·40	293	D	−170–268
				C	268–

TABLE XXXIII.—SUSCEPTIBILITIES OF DIAMAGNETIC ELEMENTS (HONDA AND OWEN).

together with a few of the paramagnetic values, are plotted in Fig. 49. Owing to the temperature variations, the curve obtained can only have a rough qualitative significance; in particular it would be of little value to insert points for paramagnetic elements whose susceptibility varies considerably, as it may do if they follow approximately a Weiss or Curie law.

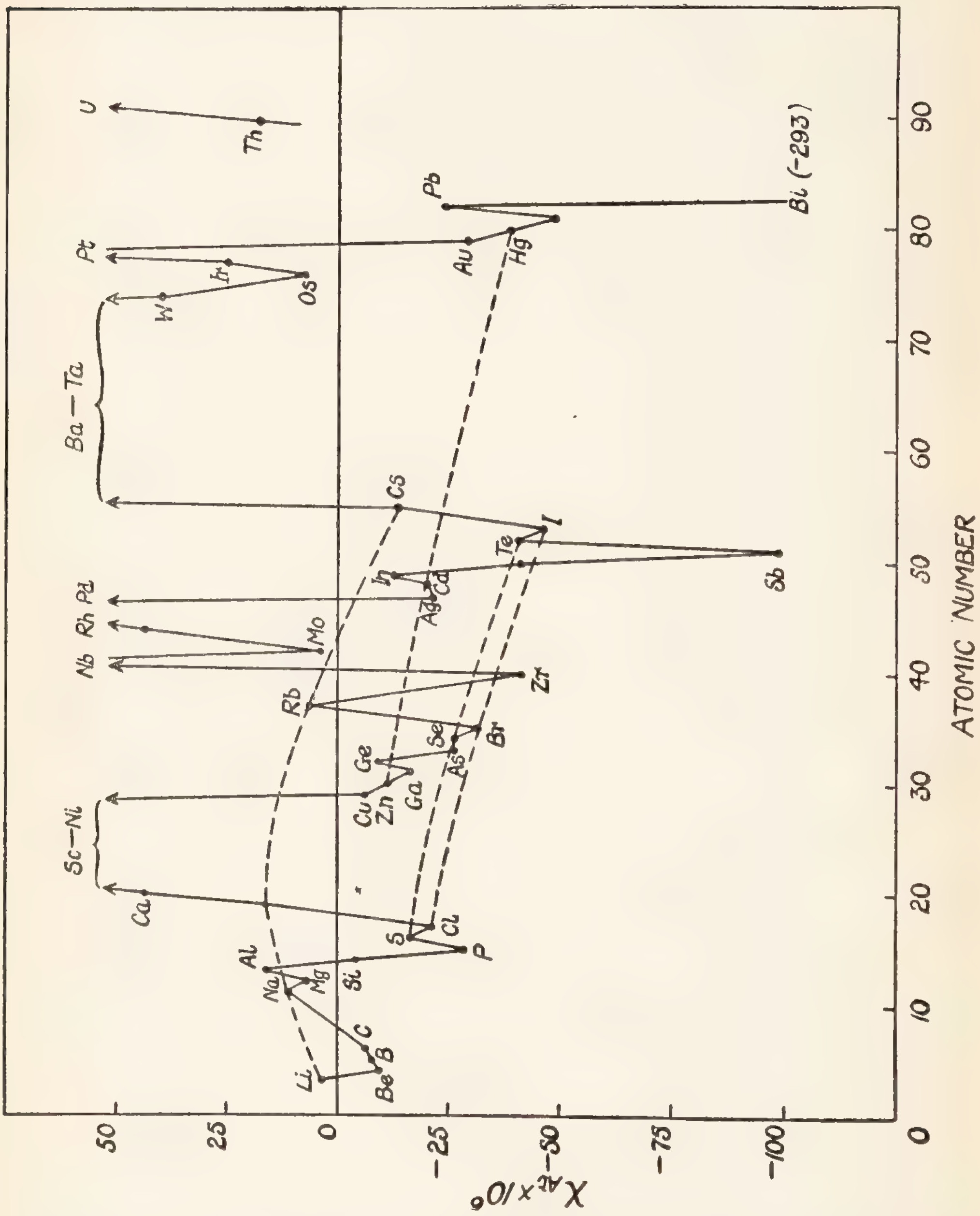


FIG. 49.—Gram-atomic Susceptibilities of Elements at Room Temperature.

Different allotropic forms of carbon gave values which differed considerably, and there were erratic variations with temperature. Impurities probably have a marked effect. The value given is that for diamond, and it will be noticed that it agrees with the value deduced by Pascal from organic liquids (Table XXXII). The different forms of sulphur had approximately the same susceptibility. The diamagnetic tin is the grey variety, the white tetragonal variety being weakly paramagnetic.

There is frequently a change in the susceptibility of diamagnetic elements at the melting-point (this behaviour contrasts with that of paramagnetics); but it varies widely both as to magnitude and sign for different elements. Elements belonging to the same family, however, seem to behave similarly. On melting, Bi and Sb decrease in susceptibility, as also Te and Pb; Ag and Au, on the other hand, increase slightly. Liquid tin is slightly diamagnetic ($\chi \doteqdot -{\cdot}04 \times 10^{-6}$).

It will be noticed in Table XXXIII that the order of magnitude of χ does not vary very greatly; a fact which supports the general diamagnetic theory. For purposes of rough comparison, the atomic weight may be taken as twice the atomic number, so that if n is the number of electrons the atom contains

$$\chi_A \doteqdot 2n\chi$$

Substituting in (4.1)

$$-10^6\chi \doteqdot \frac{1}{{\cdot}351 \times 2}(\overline{r_1^2} \times 10^{16}) \doteqdot 1{\cdot}4 \times \overline{r_1^2} \times 10^{16}$$

Values of the root mean square radius of the electronic orbits in the atom ranging from 0·1 to 1·0 A.U. will then give values for $-10^6\chi$ ranging from ·014 to 1·4 approximately, as are actually observed. Although the periodic curve (Fig. 49) does not show up any immediate and strikingly simple relations, a few regularities emerge when attention is confined to members of a single family. There seems then to be a tendency for the atomic diamagnetic susceptibility to increase with atomic number. This is shown in Cl, Br, I; S, Se, Te; Zn, Cd, Hg (as indicated by the dotted lines), and also in Cu, Ag, Au. As seems anomalous in the P–Bi series, but the values for it are somewhat uncertain; Sb and Bi are striking in the high values for their susceptibilities, which, however, are not outside the range indicated by theory.

The fact that the atoms of Cu, Ag and Au, which the Gerlach and Stern experiments show to possess a magnetic moment, build up diamagnetic crystals is of considerable interest. Any residual paramagnetic effect of the valence electrons, which presumably form the binding links in the crystal edifice (as discussed in connection with anomalous paramagnetism in Ch. VII, sect. 3), must be very small. In Li, Na and K this residual effect more than counterbalances the underlying diamagnetism. K, Rb and Cs, however, show the same variation in susceptibility with atomic number as the purely diamagnetic S and Cl families (see Fig. 49), so that Cs is diamagnetic; owing to the larger number of electrons it contains, the diamagnetic effect is stronger than any residual paramagnetic effect exerted by the valence electron.

It seems not improbable that variations in diamagnetic susceptibility with temperature are partly to be explained as arising from variations in residual paramagnetic effects, which, as has been pointed out, may increase or diminish. It must be emphasized that experiments on the elements do not enable direct quantitative deductions to be made as to the susceptibilities of the atoms themselves. The atomic constants arrived at are characteristic of the atoms when combined together in some particular way. That the values depend on the crystal structure is shown strikingly in the case of tin. Definite ionic values can be obtained from the study of solutions of diamagnetic salts, and there is room for much further work in this direction. The investigation of solids, elementary or otherwise, and the interpretation of the results, is bound up with the problems of crystal structure. The difficulties in connection with the susceptibilities of elements are certainly considerable; but, although only the fringe of the problem has here been qualitatively touched on, there are indications that much of the apparently erratic behaviour is not necessarily so incompatible with general atomic and magnetic theory as it seems at first sight.

3. Gases

The diamagnetic gases present a difficult experimental problem, partly owing to the extremely low values of their volume susceptibilities, and partly owing to the necessity of obtaining the gases in a high degree of purity. Traces of oxygen will completely invalidate the results. Until quite recently even the sign of the susceptibility of nitrogen was doubtful.

Some very careful measurements were made by Soné (1920). A Gouy method was employed, a cylindrical glass tube, divided into two compartments by a horizontal partition, attached to a special balance, being suspended vertically, with the partition midway between the poles of the electromagnet. With one of the compartments filled with air, the other with water, the susceptibility of air relative to water was first determined. For water the standard value $\chi = - \cdot 72 \times 10^{-6}$ was taken. With one of the compartments filled with the gas under investigation, the other was filled with air, or could be exhausted. The susceptibility of the gas could be determined relative to air, or to a vacuum. A Weiss electromagnet, with a 1 cm. interpole gap, was used, the fields ranging from 12 to 22 kilogauss. Experiments were made on "pure" nitrogen, prepared by heating NH_4Cl and KNO_2, and also on nitrogen derived from air (N_2^a) by removing the oxygen, and so containing argon and traces of other gases. For oxygen the results agreed fairly well with those of Bauer and Piccard (see Table VIII, Ch. VI). For the diamagnetic gases the values obtained are shown in the following table, in which κ is the volume susceptibility reduced to 0° C. and 760 mm., χ and χ_M the mass and molecular susceptibilities.

	$-\kappa \times 10^{10}$.	$-\chi \times 10^6$.	$-\chi_M \times 10^6$.
H_2 . .	1·78	1·98	4·0
N_2 . . .	3·3	·265	7·4
N_2^a . .	4·5	·360	10·1
CO_2 . .	8·3	·423	18·7

TABLE XXXIV.—SUSCEPTIBILITIES OF GASES (SONÉ).

The values obtained are of an order which is theoretically reasonable. By a consideration of the results for pure nitrogen, and nitrogen from air, as well as from those for air, nitrogen and oxygen, Soné deduced the following values for argon:

$$\text{A} \quad -10^{10}\,\kappa = 100. \qquad -10^6\chi = 5\cdot86. \qquad -10^6\chi_A = 234.$$

For helium Tänzler (1908) found

$$\text{He} \quad -10^6\chi_A = 46.$$

It was shown by Pauli (1920) that these values for the inert gas susceptibilities were far too large to be compatible with the supposed sizes of the atoms. From (4.1), with $n = 2$ for He, and $n = 18$ for A, the root mean square radius of the electronic orbits would be 2·82 and 2·11 A.U. for He and A respectively; these values are much greater than those suggested by the Bohr theory (which gives $r = \cdot 53$ A.U. for the normal hydrogen orbit), or indicated by other evidence.

The question of the susceptibilities of the inert gas configurations was elegantly treated by Joos (1923). Consider the argon atom with 18 electrons. It has the same electronic configuration as the K^+ and Cl^- ions; in passing through the series Cl^-, A, K^+, however, the ionic (or atomic) susceptibility should decrease as a result of the decrease in size of the electronic orbits owing to the increasing nuclear charge. If Z is the effective nuclear charge, then for orbits characterized by the same quantum numbers, $\overline{r_1^2} \propto \frac{1}{Z^2}$ (see V, 20, 21). As a sufficiently close approximation, therefore, from (1)

$$\chi_{K^+} : \chi_{Cl^-} = \frac{1}{19^2} : \frac{1}{17^2}$$

Now the molecular diamagnetic susceptibility of KCl is 35×10^{-6}; from this may be deduced values for the ionic susceptibilities of Cl^- and K^+, and by interpolation a value for A. Values deduced by Joos from the measurements on diamagnetic salt solutions, and the interpolated values for the inert gases, are given in the next table, and shown graphically in Fig. 50. In Table XXXV the helium value is calculated as $(3/2)^2$, that of Li^+.

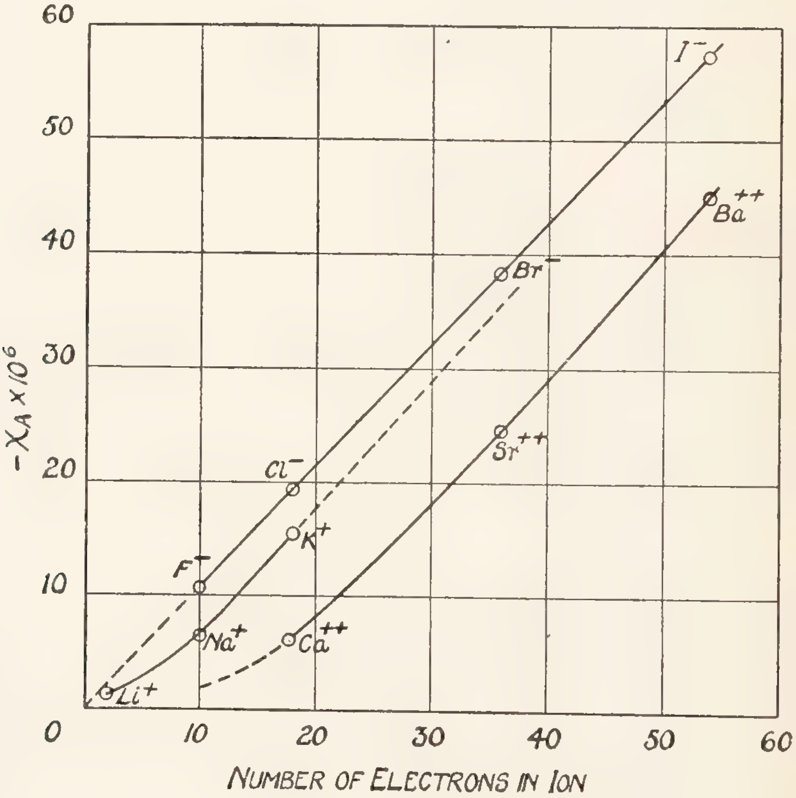


FIG. 50.—Ionic Diamagnetic Susceptibilities.

$n = 2$.	$n = 10$.	$n = 18$.	$n = 36$.	$n = 54$.
	F^- 10·8	Cl^- 19·5	Br^- 38·3	I^- 57·5
(He 3·0)	(Ne 8·8)	(A 17·5)	(Kr)	(X)
Li^+ 1·3	Na^+ 6·8	K^+ 15·5	Rb^+	
	Mg^{++}(8·6)	Ca^{++} 6·0	Sr^{++} 24·5	Ba^{++} 45·2

TABLE XXXV.— $-\chi_A \times 10^6$ FOR IONS (JOOS).

The linear character of the curves of Fig. 50 is noteworthy. For the $F^- - I^-$ series the ionic susceptibility is closely given by

$$-10^6\chi_A = 1{\cdot}07n,$$

indicating, from (4.1), a practically constant value for $\sqrt{\overline{r_1^2}}$ of ·61 A.U. For the inert gases the interpolated susceptibilities in Table XXXV give for $\sqrt{\overline{r_1^2}}$, ·72, ·55 and ·58 A.U. for He, Ne, and A respectively. (The root mean square of the radii of the projected orbits in a plane perpendicular to the field—$\sqrt{\overline{r^2}}$ in equation 1—will be ·81 times as great.)

A direct determination of the susceptibilities of the inert gases was obviously desirable, and this has recently been made by Wills and Hector (1924). A method of the Quincke type was employed, the gas at considerable pressure being balanced magnetically against a solution of known susceptibility. Using a solution containing a paramagnetic salt ($NiCl_2$) the balance could be obtained either by varying the pressure of the gas, or by varying the common temperature of the gas and solution. A solution magnetically neutral at a temperature θ was made up, and its susceptibility at any temperature could be found from Curie's law. A sketch of the essential parts of the apparatus is shown in Fig. 51; for details as to the technique and the calculation of the results, reference must be made to the original papers.

The apparatus is constructed on the O-tube principle. The solution is placed in the C—F portion, the electromagnet being applied to the meniscus at F. Solutions of $NiCl_2$ of various strengths were used, and pressures of the gases ranging from about 200 to 1,000 cm. mercury. The gas inlet is at I, and M leads to a manometer. Instead of observing the meniscus at F, the microscope was focused on gum-mastic particles in the solution at the constricted portion G of the tube. This "indicator" was very sensitive as to any movement of the meniscus on the application of the field. From observations on the pressure of the gas required for balance at a given temperature, or the temperature required at a given pressure, with a solution of definite strength, the susceptibility of the gas could be found. Elaborate precautions were taken to ensure the purity of the gases used. As a test of the apparatus the susceptibility of oxygen was measured, with satisfactory results (see Table IX). For the diamagnetic gases the results are shown in the next table:

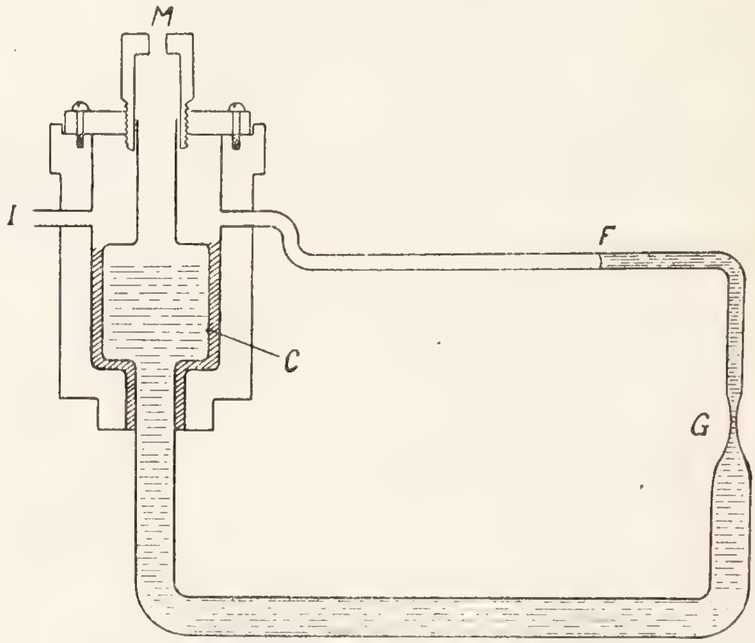


FIG. 51.—The Magnetic Balance Apparatus of Hector and Wills.

	$-\kappa \times 10^{10}$.	$-\chi_M \times 10^6$.
H_2	1·70	3·74
N_2	4·91	10·8
He	·78	1·7
Ne	2·77	6·1
A	7·52	16·5

TABLE XXXVI.—SUSCEPTIBILITIES OF GASES (HECTOR AND WILLS).

For H_2 and N_2 the values agree quite well, considering the difficulties, and the differences in the methods, with those of Soné. The inert gas susceptibilities are in excellent agreement, as to order of magnitude, with the deductions of Joos. They give for $\sqrt{\overline{r_1^2}}$, for He, Ne and A, ·55, ·46 and ·57 A.U. There is here a triumph both theoretical and experimental; for in testing —and confirming—the general theory by experiment, technical difficulties of no mean order had to be overcome. The significance of the results will be discussed further in Chapter XIV.

4. Diamagnetic Orientation

The variation in the susceptibilities of some diamagnetic gases with pressure has been investigated by Glaser (1924) with some very interesting results. For the paramagnetic gas oxygen, the work of Bauer and Piccard, together with that of Onnes, shows that there is proportionality between volume susceptibility and pressure, except for relatively slight disturbing effects probably due to the molecular field; for diamagnetic gases also the investigations of Wills and Hector show that the proportionality holds. In all these experiments, however, the pressure was considerable, usually greater than atmospheric; in Glaser's work measurements were made at much lower pressures, at which the effects of collisions would be less marked.

A very sensitive method has necessarily to be employed. That adopted was suggested by Wien. A small paramagnetic rod (volume susceptibility κ_0, volume v) was suspended by a delicate quartz fibre in a non-homogeneous field. Let κ_r be the susceptibility of the surrounding gas. Then, for the couple G acting on the rod (cf. II, 35)—

$$G = (\kappa_0 - \kappa_r) \int \tfrac{1}{2}(\nabla H^2 \times \mathbf{r})dv \quad . \quad . \quad . \quad . \qquad (5)$$

Let a_r be the angle through which the torsion head must be turned to restore the rod to its zero position, and C the torsional constant (torque per unit twist) for the fibre.

$$G = -Ca_r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5{\cdot}1)$$

C can be readily determined; moreover, for constant conditions as to the field and test piece, the integral in (5) is constant, so that, putting $C \Big/ \int \tfrac{1}{2}(\nabla H^2 \times \mathbf{r})dv = c$,

$$\kappa_r = \kappa_0 + ca_r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5{\cdot}2)$$

Let a_0 be the angle corresponding to a vacuum, a_1 to a gas of known susceptibility, a_2 to the gas investigated,

$$0 = \kappa_0 + ca_0 \qquad \kappa_1 = \kappa_0 + ca_1 \qquad \kappa_2 = \kappa_0 + ca_2 \quad (5{\cdot}3)$$

From (5.2) and (5.3)

$$\kappa_2 = \kappa_1 \frac{a_2 - a_0}{a_1 - a_0} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5{\cdot}4)$$

Relative measurements only were made, and the results of Soné and Wills and Hector for H_2, N_2 and CO_2 at definite pressures were taken as standards for κ_1. The susceptibilities of the gases at any pressure could then be found from observations of α_0 and α_1, and of α_2 at the pressure required.

Owing to the temperature variation in the paramagnetism of the test piece—the effect of a change of ·1° C. was quite noticeable—it was necessary to maintain the temperature as constant as possible. A thermocouple galvanometer arrangement, sensitive to a change of less than ·0075°, was used, and the temperature was kept constant to a few hundredths of a degree by an automatic water thermostat. A bismuth spiral served as a control of the constancy of the magnetic field, whose strength could be varied from about 2,500 to 4,500 gauss. The torsion angle was determined at successive pressures by pumping the gas out of the apparatus after filling it at a pressure slightly greater than atmospheric, and also in the inverse order, so that any Joule-Thomson heating or cooling effects would be shown up.

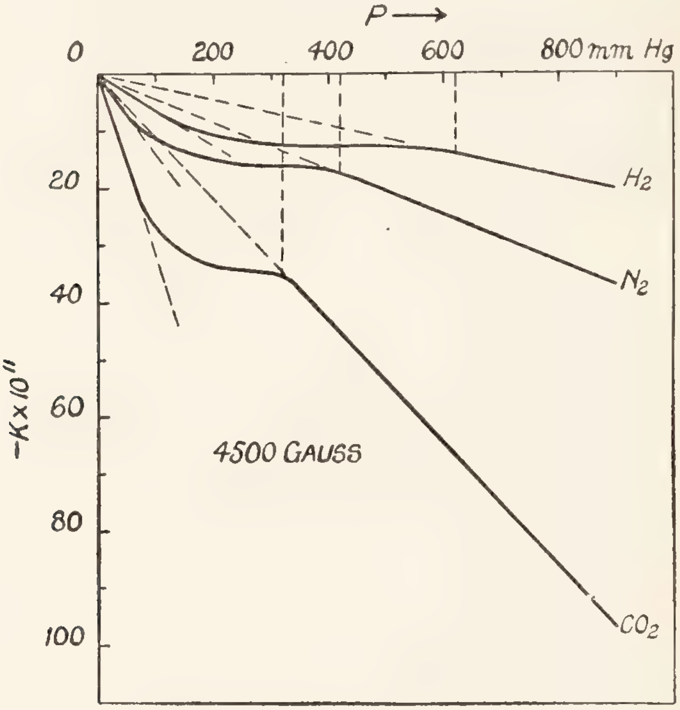


FIG. 52.—Variation with Pressure of the Volume Susceptibility of H_2, N_2 and CO_2.

The results obtained with a field of 4,500 gauss are shown in Fig. 52.

The curves are linear at the higher and lower pressures, with an intermediate connecting portion. The proportionality factor between the susceptibility and the pressure is approximately three times as great for all the gases at the lower pressures, which means that the molecular susceptibility is three times as great also. It seems impossible to interpret this surprising result otherwise than by supposing that there is a tendency for some form of orientation to occur in the field. It must be supposed, further, that this orientation is disturbed by collisions, and that it is not instantaneous, but only occurs completely when the time required is short compared with the mean time between collisions. The time apparently decreases with increase of field, for the pressure corresponding to divergence of the curve from linearity at the higher pressures increases with increase of field; occurring for CO_2 at about 260, 280 and 310 mm. Hg for fields of 2,700, 3,800 and 4,700 gauss respectively. Further, as will be seen from Fig. 52, the critical pressure is smaller the higher the molecular weight, being, at 4,700 gauss, 610, 410 and 310 mm. for H_2, N_2 and CO_2; suggesting that the time required for the establishment of orientation is greater the greater the moment of inertia of the molecule.

Though there is coherence in these qualitative considerations, serious difficulties are encountered when the attempt is made to add quantitative precision. Any "static" molecular orientation is incompatible with the values of the specific heats at the temperature at which the experiments were made; the problem is essentially similar to that arising in connection with the quantum theory of the paramagnetism of oxygen, discussed previously (Ch. VII). There is a further difficulty in accounting for the ratio of 3 to 1 for the low- to the high-pressure molecular susceptibility. This will be briefly discussed.

Consider the diamagnetism corresponding to a single electronic orbit, supposed circular, for simplicity, and of radius a. Let θ be the angle between the normal to the orbit and the field direction; let ϕ be the azimuthal angle of the electron in its orbit. The diamagnetism corresponding to the orbit, from (1), is then given by

$$\chi_\theta = -\frac{e^2}{4mc^2}\overline{r^2} = -\frac{e^2}{4mc^2}a^2\left[\frac{1}{2\pi}\int_0^{2\pi}(\cos^2\phi\cos^2\theta + \sin^2\phi)\,d\phi\right] \qquad (6)$$

$$= -\frac{e^2}{4mc^2}\frac{a^2}{2}(1 + \cos^2\theta) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6.1)$$

For an electronic orbit with its plane perpendicular to the field ($\theta = 0$) the susceptibility is thus twice as great as for one with the plane parallel to the field $\left(\theta = \frac{\pi}{2}\right)$. For a number of orbits orientated at random the mean susceptibility is given by

$$\chi_r = -\frac{e^2}{4mc^2}\cdot\frac{a^2}{2}\cdot\frac{\int_0^{\frac{\pi}{2}}(1+\cos^2\theta)\sin\theta d\theta}{\int_0^{\frac{\pi}{2}}\sin\theta d\theta}$$

$$= -\frac{e^2}{4mc^2}\cdot\frac{2a^2}{3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6.2)$$

For the ratio between the susceptibilities for all the orbits perpendicular ($\chi_\perp$) and parallel to the field ($\chi_{\parallel}$) and orientated at random (χ_r)

$$\chi_{\parallel} : \chi_r : \chi_\perp = \tfrac{1}{2} : \tfrac{2}{3} : 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (6.3)$$

If the electrons in atoms moved in orbits whose planes were parallel, orientation might account for an increase in diamagnetic susceptibility of $\frac{3}{2}$; so that even in this, the most favourable case, the increase would only be half as great as that actually observed.

For molecules the problem becomes more complicated. A magnetic field does not give rise to a uniform precession of a molecule as a whole, the ratio of mass to charge being different for the nuclear and electronic constituents. Practically the whole of the diamagnetic effect will be due to the electronic precession. This, presumably, for the inner electrons, is about the individual nuclei; for the outer shared electrons the motion will be very complicated. It may be referred to as "molecular electronic precession." It seems not impossible that the constraints which molecular stability necessarily entails prevent any molecular electronic precession except about some definite axis. If this were so, only the field along the axis would be effective; the ratio of the susceptibility due to shared electrons for the axes orientated at random to that for the axes parallel to the field would then, since the induced moment is proportional to H cos θ, be given by

$$\chi_r' : \chi_{\parallel}' = \mathrm{H}\,\overline{\cos\theta.\cos\theta} : \mathrm{H} = \tfrac{1}{3} \quad . \quad . \quad . \quad (7)$$

It seems unlikely that Glaser's results can be explained in this way, if the axis is taken as that joining the nuclei; for it would be necessary to suppose that there was an alignment of the molecular axes parallel to the field at low pressures; and this is incompatible with the values for the molecular heats (for

H_2, 4·8 at 22° C.) and the quantum values for the rotational energy (which is small compared with kT). At ordinary temperatures practically all the molecules must be in rotation. If, however, the axis of the molecule about which precession can occur is taken as the axis of rotation of the nuclei, some of these difficulties are removed. This will be discussed further in Chapter XV.

Whether molecules (or atoms) as a whole orientate in a field, or only particular electronic orbits, remains an open question. It does not seem to have been considered whether the molecular heat of oxygen, or of diamagnetic gases at low pressures, is influenced by a magnetic field, and although it seems very unlikely, it might be worth while to test this experimentally. If it is the nuclear rotational axis which aligns itself in the field direction, no effect would be expected.

It would be unprofitable to discuss these speculative issues further at present. The results of Glaser's projected more precise investigations not only on molecular, but also on atomic gases, will be awaited with great interest.

Foëx and Royer (1925) have obtained some results on substances which pass into a " nematic " or fibrous state, which they have also interpreted in terms of diamagnetic orientation. Para-azoxyanisol may be considered. As an isotropic powder the substance has a constant diamagnetic susceptibility up to 116° C., when it passes into a nematic state ; its susceptibility decreases suddenly by about 17 per cent., then increases until the melting-point is reached (134° C.), the liquid having again a constant susceptibility approximately the same as that of the powder. On cooling, the nematic state can be maintained down to 95° C. ; the smallest nematic susceptibility observed is about 18 per cent. less than that of the liquid. If it is assumed that in the nematic state the electronic orbits are orientated parallel to the field, and in the liquid state at random, from (6.3)

$$\frac{\chi_l - \chi_n}{\chi_l} = \frac{\frac{2}{3} - \frac{1}{2}}{\frac{2}{3}} = \frac{25}{100} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

As thermal agitation may disturb the orientation, even in the nematic state, the experimental result is in fair agreement with the hypothesis. The interpretation is interesting, but can hardly be regarded as conclusive, particularly as in Glaser's experiments the smaller susceptibility corresponds to random orientation.

5. Oxley's Work. Intrinsic Fields in Diamagnetics

It will be convenient to give a brief sketch of some of Oxley's work here, for, although his investigations have extended over a wide range of magnetic phenomena, many of his conclusions are of particular interest in connection with diamagnetism.

The susceptibilities of some forty organic substances were measured over a range of temperatures from − 180° C. to 200° C. For aliphatic compounds the change on melting was small. When aromatic liquids were supercooled into a vitreous state there was no appreciable change; but on crystallization there was a decrease in the diamagnetic susceptibility, which was generally of the order of 5 per cent. Melting the crystals resulted in a corresponding increase. This is attributed by Oxley to large local molecular fields between the molecules in diamagnetic crystals; to account for the observed susceptibility changes, Oxley concludes that the fields, if magnetic, must be of the order of 10^7 gauss. The precise reasoning, however, is somewhat obscure. In a diamagnetic, the electronic orbits balance magnetically in the absence of an external field. If μ is the moment of an individual electronic orbit, τ the period of the electron, from (1), making use of (II, 59),

$$\frac{d\mu}{\mu} = -\frac{H\tau e}{4\pi mc} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

This will be of the order -10^{-9} H. Internal fields of the order 10^7 would therefore give rise to fractional changes in the moments of the individual electronic orbits of the same order as the fractional changes in diamagnetic susceptibility in passing from the liquid to the crystalline state. A field, however, gives rise to precession without change in the area of the orbit; the diamagnetism depends only on the area of the orbit (1); for this reason alone, therefore, it would seem that the changes in susceptibility cannot be ascribed to local purely magnetic fields. If the general diamagnetic theory is correct, the only definite conclusion that can be drawn from the observations is that the mean projected area of those electronic orbits which are free to precess is less in crystals than in liquids. This implies that there are forces between the molecules which are appreciable in crystals, though their precise nature may be indeterminate. From an energy point of view, as was discussed in connection with Weiss's theory, it is immaterial whether the fields are treated as magnetic or not, provided that a uniform procedure is adopted. Thus, having assumed that the changes in susceptibility are due purely to intrinsic magnetic fields, it is possible to find the difference in energy per unit volume of the substances investigated in the crystalline and liquid form, and hence to calculate the latent heats of fusion, assuming the energy to be magnetic and using the values for the internal fields deduced from the susceptibilities. In this way Oxley calculates that the latent heats of fusion should be of the order of 25 calories; for a considerable number of substances experiments give values ranging from 21 (aniline) to 35 calories (naphthalene). From the potential energy per unit volume it is further possible to calculate the tensile strengths of crystals. That calculation and experiment agree reasonably well shows that the decreased susceptibility of a crystal compared with a liquid is closely related to its increased internal potential energy; but it does not necessarily show that this energy is magnetic.

In connection with his studies on the relation of magnetism to the crystalline state, Oxley called attention to and extended some earlier work of Tyndall on the deportment of para- and dia-magnetic crystals in a magnetic field. An ordinary paramagnetic rod sets itself axially, that is, parallel to the field, a diamagnetic rod equatorially. With crystals, however, the setting seems to be determined rather by the direction of the crystal axes than by the shape of the specimen as a whole. $NiSO_4$ (para-) sets itself with the crystal axis axial, and $MgSO_4$ and $ZnSO_4$ (dia-) with their crystal axes equatorial. Beryl, however, also sets itself with its axis equatorial although it is paramagnetic. Oxley explains this anomalous behaviour by the fact that the cleavage plane in beryl is perpendicular to the crystal axis, while parallel in the other crystals; so that, as a general rule, it may be stated that paramagnetic crystals set themselves with their cleavage planes parallel to the field, diamagnetic crystals with their cleavage planes perpendicular to the field. Naphthalene is diamagnetic (it is repelled in a non-homogeneous field), and individual thin plates, obtained by cleavage, set themselves equatorially. Oxley constructed a pile of about 80 thin plates whose length, perpendicular to the plates, was 1·75 times its breadth. The specimen as a whole set itself axially, so, in agreement with the above rule, with the individual plates (and hence the cleavage planes) perpendicular to the field. The atoms, or ions, in crystals are most closely packed in the cleavage planes; paramagnetics therefore seem to set so that the atoms are as close together as possible in the field direction, and diamagnetics so that they are as far apart as possible; but without experiments as to how far the susceptibility is a function of direction in a crystal, it does not seem possible to draw any further definite conclusions. The observations, however, certainly suggest that the forces determining the cleavage planes are partly magnetic in origin.

From his work as a whole Oxley concluded that magnetic phenomena could not be accounted for by atoms of the Bohr type, with large electronic orbits ; he inclined rather to a picture of the atom (or molecule) in which the electrons rotated in small orbits about the mean positions assigned to them in the Lewis-Langmuir static models. This seemed necessary to account for the large values of the local fields, assumed to be magnetic, between the molecules ; these fields, as has been seen (Ch. V), being in general much larger than those which would arise from Bohr orbits. There is, however, such an enormous mass of evidence in favour of the general Bohr theory, and it accounts with such remarkable success for so many magnetic phenomena, that it is out of the question to abandon it. Moreover, the difficulty as to the magnitude of the molecular fields assumes quite a different significance as soon as the supposition is abandoned—as it must be—that the fields are purely magnetic. There are certainly many difficulties, but, in the light of the discussion which has been given of intrinsic fields in paramagnetics, it seems undoubted that for these and for diamagnetics also, a solution will eventually be found in terms of the general quantum theory.

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CHAPTER XIII

MISCELLANEOUS MAGNETIC EFFECTS

1. The Joule and Related Effects

MAGNETIZATION is generally accompanied by slight mechanical deformation. Investigations have been almost entirely confined to ferromagnetics, the simplest phenomenon being the change in length of a rod subjected to a magnetic field. This was first observed, for iron, by Joule (1847). The curves of Fig. 53 give an indication of the nature and magnitude of the effect for different substances.

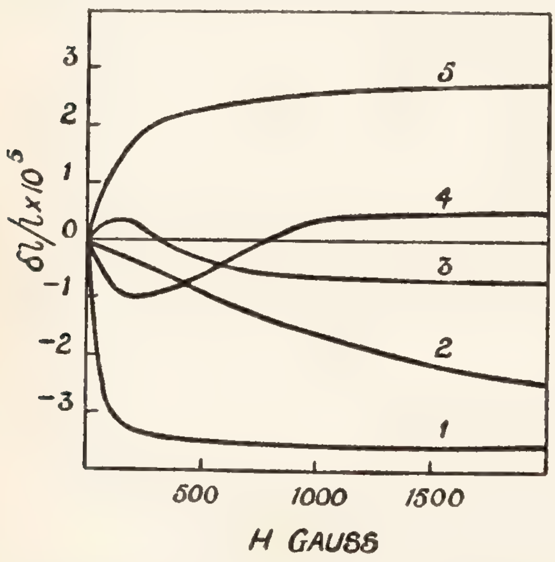

FIG. 53.—Change in Length of Ferromagnetic Rods in a Magnetic Field.

1. Nickel. 2. Annealed Cobalt. 3. Steel. 4. Cast Cobalt. 5. Ni-Fe Alloy (6 per cent. Ni).

With large fields there is no change in length. Nickel decreases in length with increasing field, while iron at first increases and then decreases, eventually becoming shorter than in its unmagnetized state. Iron-nickel alloys increase in length. The form of the curves depends markedly on the thermal treatment the specimens have received (and so, essentially, on their crystalline nature), on the temperature and other influences, and any coefficients which are found can only be regarded as exactly characteristic of an individual specimen under particular conditions.

The fact that magnetization produces a change in length suggests that a longitudinal pull or compression will produce a change in magnetization. The magnitude of this Villari effect can be at least roughly calculated from the Joule coefficients if the elastic constants of the specimen are known. The magnetization of nickel is increased by longitudinal compression, decreased by extension. Iron, which shows a Joule reversal, also shows a Villari reversal, its magnetization being increased by extension in weak fields, and decreased in strong. The reciprocal relations break down if the strains are considerable.

Accompanying the longitudinal changes there are changes in the transverse dimensions on magnetization, and in general changes in volume. The volume changes have been investigated in particular by Nagaoka and Honda. The volume of iron is increased, that of cobalt decreased.

A number of other phenomena may be regarded as special cases of the Joule and Villari effects. The superposition of a longitudinal and a circular magnetic field (due to a longitudinal electric current) produces a twist (Wiedemann effect); while a twist superimposed on a circular field influences the longitudinal magnetization.

A general energy-thermodynamic treatment enables reciprocal relations to be deduced involving magnetic and elastic constants. Although these relations are useful in indicating an appropriate form in which to set forth experimental results, and in showing whether different effects are fundamentally distinct, they shed no light on the underlying physical processes.

Although an enormous amount of experimental work has been done, from the point of view of theoretical interpretation, it practically all suffers from the disadvantage that it has been necessarily made on specimens which consist of masses of small crystals, of indeterminate size, distributed more or less at random. Before it is possible to make much advance in a clear understanding of the inter-atomic or molecular forces to which the various magneto-mechanical effects must ultimately be due, it is necessary to have some idea of the effects in single individual crystals. In this connection some results of Webster are of particular interest. He has found that with iron crystals the change in length depends on the direction of magnetization; along one axis there is a decrease, and along an axis at right angles an increase. The form of the curves is such as would give a resultant curve, for crystals orientated at random, of the type shown in Fig. 53.

It has seemed reasonable (cf. Ch. VII, sect. 3) to suppose that in ferromagnetic (and paramagnetic) crystals there are magnetic ions free to reorientate in the skeleton-like structure built up by the "shared" electrons, the lattice of the crystal being primarily determined by these. The Weiss molecular fields, and intrinsic fields generally, are then not regarded as purely magnetic fields (which they cannot be); although the magnetic ions exert a powerful mutual effect on each other, this is not direct, but occurs through the intermediate shared-electron structure. The reorientation of the ions consequent on magnetization will distort this structure. For the ions themselves the resultant effect will be equivalent to that of a magnetic field. For the crystal as a whole, which will undergo changes in dimensions, the resultant effect will be equivalent to that of a mechanical stress. Although the picture is crude, it seems not unreasonable. The atomic mechanics of crystals is as yet little developed, though its foundations have been laid by Born and Landé and others. The magneto-mechanical properties of crystals present a wide field for future theoretical and experimental research.

2. Galvanomagnetic and Thermomagnetic Phenomena

In 1878 Hall observed that when a current-bearing conductor was placed in a magnetic field, the lines of force being at right angles to the current, a transverse potential difference was set up. Since then an enormous amount of experimental work has been carried out on this and allied effects, but, theoretically, few phenomena have been more baffling. The behaviour of different substances, and of the same substance under different conditions, varies in such an apparently erratic manner that it is impossible to summarize the results usefully, and reference must be made to Campbell's comprehensive monograph (1923). The general nature of the phenomena only can be briefly sketched.

Let I be the current in a plate of width b, and thickness d, and let H be the strength of the magnetic field at right angles to the current and the width of the plate. The total transverse electromotive force set up, E, is proportional to the width of the plate, to the field strength, and the current density I_a. For the electromotive force per unit width, with R as the Hall coefficient,

$$\left.\begin{aligned} \frac{E}{b} &= RHI_a = RH\frac{I}{bd} \\ E &= \frac{RHI}{d} \qquad R = \frac{Ed}{IH} \end{aligned}\right\} \qquad (1)$$

As an example, for a gold plate, with $d = \cdot 1$ mm., $I = 2$ amp. ($= \cdot 2$ Abs.), $H = 10{,}000$ gauss, $E = 1\cdot 40 \times 10^{-6}$ volt (140 Abs.), so that

$$R = \frac{140 \times \cdot 01}{10{,}000 \times \cdot 2} = \cdot 0007.$$

The Hall effect can be considered as a rotation of the equipotential lines through an angle ϕ given by

$$\tan \phi = \frac{\mathrm{RH}}{r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where r is the specific resistance of the substance. With the current flowing from left to right, R is then counted as positive if the equipotentials rotate in the same direction as the current flows in the exciting electromagnet (as in Fe, Co, Zn, Sb) and negative if in the opposite (as in Ni, Au, Bi). The Hall coefficient for a few elements at room temperature (approximate mean values to one significant figure from different observers' results) are given in the following table. The elements are grouped in their periodic families.

Li	− ·002	Sb	+ ·1
Na	− ·003	Bi	− 9
Cu	− ·0005	Te	+ 500
Ag	− ·0008		
Au	− ·0007	Fe	+ ·01
		Co	+ ·002
Zn	+ ·0008	Ni	− ·01
Cd	+ ·0006	Pd	− ·001
		Pt	− ·0002
Sn	− ·00003		
Pb	+ ·00009		

TABLE XXXVII.—HALL COEFFICIENTS AT ROOM TEMPERATURE.

The prediction of the simple "electron gas" theory of electric conduction for the Hall coefficient gives a standard of reference as to orders of magnitude. Assuming that there are n "free electrons" per unit volume, whose motion, between collisions, depends on the temperature, and the electric and magnetic fields, Richardson deduced

$$\mathrm{R} = +\frac{2}{3}\frac{1}{ne} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Let ϱ be the density of the substance, A the atomic weight, p the number of free electrons per atom. (3) may be written

$$\mathrm{R} = +\frac{2}{3}\frac{\mathrm{A}m_{\mathrm{H}}}{p\varrho e}$$

$$\fallingdotseq -7 \times 10^{-5}\frac{\mathrm{A}}{p\varrho} \quad . \quad . \quad . \quad . \quad . \quad (3.1)$$

Expressions somewhat similar to Richardson's are derived by other writers, the electronic theory having been developed most completely by Livens. It has been supposed that both positive and negative carriers are concerned in electrical conduction, but there now seems little doubt that the carriers are almost entirely electronic. (If e and m are the charge and mass of the carriers, an acceleration f will be equivalent in current effect to an electromotive force E where $Ee = mf$. Experimentally, for f/E, Tolman finds values ranging from $1 \cdot 5 \times 10^7$ to $1 \cdot 9 \times 10^7$, in close agreement with $1 \cdot 77 \times 10^7$ for e/m for electrons.) The simple theory, then, predicts a negative Hall coefficient of an order of magnitude, with reasonable assumptions as to p, ranging from about 10^{-1} to 10^{-4}. The theory is obviously quite inadequate to account for the observed results.

The differences in sign do not depend on whether the substances are para- or dia-magnetic; they must, however, in some way depend on intrinsic fields, which may oppose the external field and more than counterbalance it. A few characteristics of the Hall effect in different substances will be briefly described with a view to indicating the general nature of the requirements which more adequate theories will have to satisfy.

For most metals the Hall coefficient is practically independent of the field, though in Sb and Bi there seems to be an approach to a limiting value; in ferromagnetics, the coefficient increases rapidly at first, and then approaches a saturation value—the E.M.F. developed being approximately proportional to the intensity of magnetization, rather than to the applied field. In ferromagnetic metals the coefficient increases with temperature to a maximum in the neighbourhood of the Curie-point, and then decreases rapidly. In most non-magnetic metals there is relatively little change with temperature, but in Sb, Bi and Te there is a decrease from 0° C. to the melting-point, at which the effect is inappreciable. In Bi the effect decreases also below 0° C., and at low temperatures it may change sign and become positive. The fact that the existence of a Hall effect in liquid metals has not been established is noteworthy. Crystalline structure seems to be essential, the magnitude of the effect in Sb, Bi and especially Te, which are usually markedly crystalline, supporting this view. Wold found that in finely powdered tellurium the effect was very small. It may be further noted that in bismuth crystals the effect varies greatly in different directions, R being of the order of 10 for fields perpendicular to the principal axis, and of the order of ·4 for fields parallel. It would seem, then, that the Hall effect is a function of the intensity of magnetization rather than of the external field, and further that it depends on the intrinsic crystalline fields. It is, however, impossible to develop a theory of the Hall effect without a satisfactory theory of normal electrical conduction. Many lines of evidence indicate that the electron gas theory can no longer be maintained. In particular the experiments of Onnes on conductivity at low temperatures may be mentioned. Possibly the mechanism involved in electrical conduction is a transfer of electrons from atom to atom, shared electrons in crystals being successively displaced under the influence of the applied electric field. Whatever the nature of the process, however, it is undoubted that much light might be shed on it by extensive investigations of the conductivity of single crystals, of known structure, over as wide a range of temperature as possible; the Hall and allied effects being studied in the same specimens. Recent advances in the production of large metallic crystals lead to the hope that experiments along these lines may be pushed forward to the fullest possible extent.

If, in place of an electric current, a heat current flows through a plate, a transverse electromotive force is produced by the application of a field (Nernst effect).

Let $\frac{dt}{dl}$ be the temperature gradient along the plate, b its width, as in (1); using Q as the Nernst coefficient

$$E = QHb\frac{dt}{dl} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Let W be the amount of heat passing through a cross-section of the plate, K the thermal conductivity. Then, since $W = Kbd\frac{dt}{dl}$,

$$E = \frac{Q}{K}\frac{HW}{d} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.1)$$

$\frac{Q}{K}$ is thus analogous to R in (1). To a certain extent it is found that the variations in magnitude of $\frac{Q}{K}$ and R for different substances run parallel to each other.

Besides transverse differences of potential, transverse differences of temperature are produced by a magnetic field; and there are corresponding longitudinal effects. The various effects are conveniently symbolized by a method proposed by Hall: according as the effect is transverse or longitudinal T or L is written, prefixed by *e* for an electric, *h* for a heat current, the suffixes *e* and *h* denoting that the electric (potential difference) or heat (temperature difference) effect of the magnetic field is considered. Thus the Hall effect may be symbolized by ${}_eT_e$; the Nernst effect by ${}_hT_e$. The Righi-Leduc effect, ${}_hT_h$, is of particular interest, for, with the exception of bismuth, which behaves erratically, its sign is the same as that of the Hall effect for all metals so far examined. This indicates that the carriers of heat and electric currents are influenced in the same way by a magnetic field, and so, presumably, that electrons play a predominant part both in heat and electric conduction.

The change in resistance of a conductor in a magnetic field (${}_eL_e$ when the field is applied transversely) is of considerable practical importance, spirals of bismuth, in which the effect is large, being used for the measurement of magnetic fields (Ch. III, sect. 2). That crystal structure again plays a prominent part is indicated by the work of Becker and Curtiss (1920) who found that thin cold spluttered bismuth films (which would be amorphous) showed no increase in resistance in fields up to 15,000 gauss. For metals other than ferromagnetic, there is, in general, an increase in resistance in transverse and longitudinal fields, proportional to the square of the field strength, the magnitude of the effect in single crystals depending on the direction. Ferromagnetics also increase in resistance in longitudinal fields, the change being roughly proportional to the square of the intensity of magnetization. In transverse fields the resistance may increase slightly at first, or decrease slowly ; there is then a rapid decrease followed by an approach to a saturation value. According to the electron gas theory, the electrons, between collisions, will move in cycloidal or spiral paths, in transverse or longitudinal fields, and there should be an increase in resistance, proportional to the square of the field. Quantitatively, the theory breaks down. In ferromagnetics the resistance and magnetostrictive changes seem to be connected, but none of the relations proposed hold generally.

In this section an attempt has been made to give a brief indication of the character of a wide range of phenomena presenting innumerable problems for further investigation. Extensive experimental data have been amassed, and intensive, more specialized research is now required. Well-thought-out investigations on galvanomagnetic effects in relation to crystal structure cannot fail to shed some light on the processes involved in electrical conduction, and on the nature of intrinsic fields.

3. Magneto-caloric Effects

In this section will be briefly considered some of the thermal phenomena associated with the magnetization of ferromagnetics, in the light of the Langevin-Weiss theory (Ch. IV, sect. 3). In accordance with the first law of thermodynamics, for unit mass of a substance

$$\delta Q = \delta U - \delta A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

δQ being the heat supplied, δA the external work done on the substance, and δU the change in the specific internal energy. Suppose the work done is purely magnetic, volume changes being neglected; let σ be the specific intensity of magnetization. Then

$$\delta Q = \delta U - H\delta\sigma \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5.1)$$

U may be taken as a function of T and σ, so that

$$\delta Q = \frac{\partial U}{\partial T}\delta T - \left(H - \frac{\partial U}{\partial \sigma}\right)\delta\sigma \quad . \quad . \quad . \qquad (5.2)$$

According to Weiss's hypothesis, there is an internal molecular field proportional to the magnetization, such that (see IV, 17)

$$H_i = N\varrho\sigma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

Since

$$\frac{\partial U}{\partial \sigma}\delta\sigma = - H_i\delta\sigma \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6.1)$$

$$\frac{\partial U}{\partial \sigma} = - N\varrho\sigma \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6.2)$$

(It has already been mentioned (Ch. IV, sect. 4) that the molecular field may be formally regarded as a function of the internal energy, as these equations show, no specific hypothesis being made as to whether it is magnetic in origin; actually, however, this is simply a restatement of the problem, for the question arises as to why the internal energy depends on the magnetization in the way it does.) For the specific heat S, there results, after substituting (6.2) in (5.2),

$$S = \frac{dQ}{dT} = \frac{\partial U}{\partial T} - (H + N\varrho\sigma)\frac{d\sigma}{dT} \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

When the external field, H, is zero

$$S = \frac{\partial U}{\partial T} - N\varrho\frac{d}{dT}\left(\frac{\sigma^2}{2}\right) \quad . \quad . \quad . \quad . \quad . \qquad (7.1)$$

Now ferromagnetics below the Curie-point, according to Weiss's theory, are spontaneously magnetized throughout the extent of the elementary crystal domains, when the state is one of equilibrium; this spontaneous magnetization decreases with increased temperature, in the way shown in Fig. 18, vanishing at the Curie-point. The specific heat of a ferromagnetic will thus be greater than it would be, were it devoid of ferromagnetic properties. Above the Curie-point (7.1) reduces to

$$S = \frac{\partial U}{\partial T} \quad \dots\dots\dots \quad (7.2)$$

At the Curie-point there will be a sudden decrease in the specific heat, the magnitude depending on $\frac{d\sigma^2}{dT}$ in the immediate neighbourhood. The exact evaluation of this is difficult. The development in series of IV, 24 (derived from IV, 19 and IV, 21) gives as an approximation for $T < \theta$, with σ_0 as the saturation moment per unit mass, and σ as the spontaneous moment due to the internal field,

$$\frac{\sigma}{\sigma_0} \doteqdot \sqrt{\frac{5}{3}\left(1 - \frac{T}{\theta}\right)} \quad \dots\dots \quad (8)$$

so that

$$\frac{d\sigma^2}{dT} \doteqdot -\frac{5\sigma_0^2}{3\theta} \quad \dots\dots\dots \quad (8.1)$$

Let m be the molecular weight of the "magnetic molecule," σ_{m_0} the gram-molecular saturation moment.

From IV (28)

$$\theta = \frac{\sigma_{m_0}{}^2 N\varrho}{3mR} = \frac{mN\varrho\sigma_0{}^2}{3R} \quad \dots\dots \quad (9)$$

Substituting (9) in (8.1), there results in (7.1)

$$S = \frac{\partial U}{\partial T} + \frac{5R}{2m} \quad \dots\dots \quad (10)$$

so that at the Curie-point $\left(\text{above which } \frac{d\sigma^2}{dT} = 0\right)$

$$\triangle S_\theta \doteqdot -\frac{5R}{2m} \quad \dots\dots\dots \quad (10.1)$$

It must be stressed that (10.1) gives only a rough estimate of the order of magnitude of the change to be expected, owing to the approximations involved in (8).

Since in (5.1) H and σ play the same part as p and v respectively in the usual thermodynamic relations, in complete analogy with Clapeyron's equation, for a sudden adiabatic change $\triangle H$ in the field, writing S_H for the specific heat with constant field

$$S_H \triangle T = T\frac{\partial \sigma}{\partial T}\triangle H \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

A corresponding equation may be derived relating the change in temperature to the change in the magnetization. From (5) or (7), for an adiabatic change

$$\frac{\partial U}{\partial T}dT = (H + N\varrho\sigma)d\sigma \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Let C be the Curie constant per unit mass.

Then, from the Weiss law for paramagnetics,

$$\frac{\sigma}{H} = \frac{C}{T - \theta}$$

where
$$\theta = N\varrho C$$

Hence
$$H + N\varrho\sigma = \frac{T\sigma}{C} \quad . \quad . \quad . \quad . \quad . \quad . \quad (12.1)$$

giving
$$\frac{\partial U}{\partial T}dT = \frac{T\sigma}{C}d\sigma \quad . \quad . \quad . \quad . \quad . \quad . \quad (12.2)$$

Since $\frac{\partial U}{\partial T}$ varies little, for the increase of temperature accompanying a sudden adiabatic increase in magnetization

$$\triangle T = k\triangle\sigma^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12.3)$$

The temperature increase indicated by equations (11) and (12.3) is known as the magneto-caloric effect ; the degree of accordance between theory and experiment with respect to this, and the ferromagnetic specific heat, may be illustrated by some of the results of Weiss and Forrer for nickel (1924).

From a very extended and accurate series of measurements over a range of temperatures from 20° to 405° C., and with fields up to 21,000 gauss, the magnetic isothermals were plotted. The general nature of the curves is shown in Fig. 54.

Considering as a typical curve that for 277° C., it will be seen that the magnetization attains a large value in small fields (hysteresis effects, occurring in fields of a few gauss, are not shown up, owing to the scale employed) ; the approach to saturation, in the usual sense of the word, is represented by the hyperbolic portion of the curve, being practically attained at 5,000 gauss. With larger fields, there is an increase in magnetization proportional to the increase in the field. In terms of the Weiss theory, the first effect of the field is to change the sense of magnetization of those elementary crystals whose resolved moment is opposed to the field. (This is accompanied by hysteresis effects.) A hemispherical random distribution is assumed instead of a spherical random distribution (see IV, 30, etc.). This is followed by a gradual alignment in the field direction, corresponding to the hyperbolic part of the magnetic isothermals. Finally, the magnetization increases steadily with the field, this corresponding to a true increase in magnetization, and not merely to an apparent increase due to alignment of the moments of the elementary crystals already magnetized to the degree appropriate to the temperature and the internal field. The spontaneous magnetization corresponding to any temperature may be determined by extrapolation of the linear portion of the isothermals to zero external field, as shown by the dotted lines in Fig. 54. It is unnecessary to consider the gradual change in the nature of the isothermals in passing through the Curie-point (357° C.), which, however, may be noted in the figure. From the results, a derived curve giving the spontaneous magnetization as a function of the temperature may be drawn. From this, $\frac{\partial\sigma}{\partial T}$ at any temperature may be found.

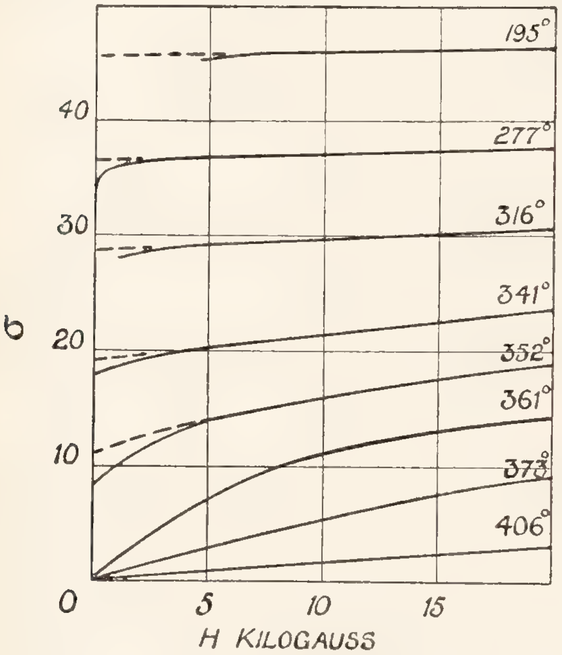

FIG. 54.—Magnetic Isothermals of Nickel. σ Specific Intensity of Magnetization.

In Fig. 55, the magnitude of the magneto-caloric temperature change (equation 11) is shown as a function of the temperature.

From (11) it is possible to calculate the specific heat (in constant field) from the purely magnetic data $\frac{\partial\sigma}{\partial T}$ and $\frac{\Delta T}{\Delta H}$;

the results are shown in curve (3). Considering the experimental difficulties, the close agreement of curve 3 with 4, obtained by direct calorimetric measurements, is very remarkable. For the change in the specific heat at the Curie-point

$$\Delta S_\theta \doteqdot \cdot 028.$$

Taking for m the atomic weight of nickel, 58·7, (10.1) gives

$$\Delta S_\theta = \cdot 085.$$

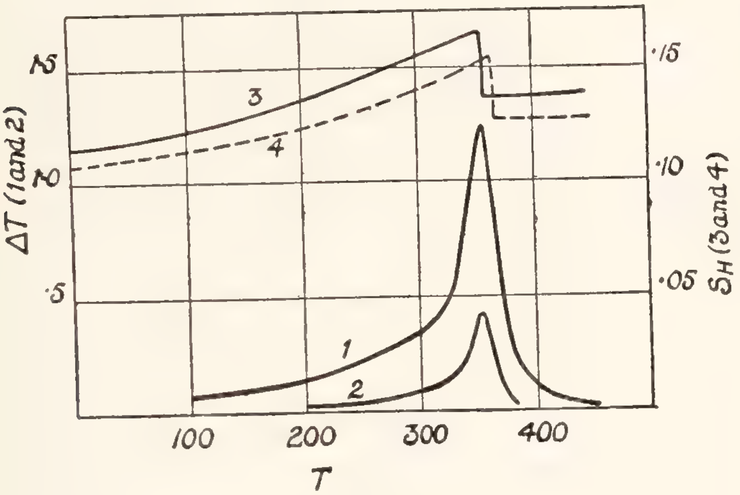

FIG. 55.

Curves 1 and 2. Magneto-caloric Effect in Nickel.
1. ΔH = 17,775 gauss.
2. ΔH = 4,160 gauss.

Curves 3 and 4. Specific Heat of Nickel.
3. From magneto-caloric effect.
4. Calorimetrically.

This suggests that the "magnetic molecule" of nickel contains more than one atom. Writing $m = nA$, from (10.1)

$$\Delta S_\theta \doteqdot \frac{4{\cdot}97}{nA} \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Close agreement with experiment is found if n is taken as 3; this is interesting in view of the suggestion which has been made (Ch. VII, sect. 2) that only 2 in every 5 nickel atoms have a magnetic moment associated with them. For iron, however, the observed change in the specific heat is ·12, which is greater than the value given by (13) for $n = 1$ ($\Delta S_\theta = \cdot 089$), so that no definite conclusions may be drawn.

Instead of plotting ΔT against the change of field ΔH, it may be plotted against the corresponding $\Delta\sigma^2$ as suggested by (12.3). It is then found that the curves have the form shown in Fig. 56.

The right-hand portion QR of the curve is linear and may be represented by

$$\triangle T = A(\sigma^2 - \sigma_0^2) \quad . \quad . \quad . \quad . \quad . \quad (14)$$

It will be clear from the considerations already advanced that σ_0 in this expression may be regarded as the spontaneous magnetization at the particular temperature. It is, in fact, only the true increase in the magnetization (and not the apparent increase) which is accompanied by the reversible magneto-caloric phenomenon. When the spontaneous magnetization is plotted as a function of the temperature, it is found that there is complete accordance between the values deduced from the magneto-caloric effect, and those deduced by extrapolation from the ordinary magnetic isothermal curves.

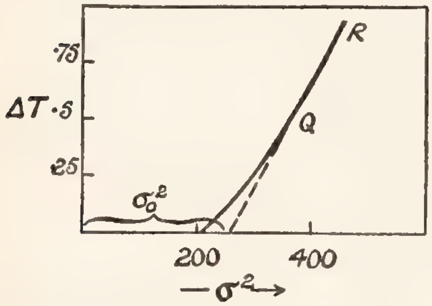

FIG. 56.—Magneto-caloric Effect in Nickel as a Function of σ^2, at 347° C.

The magneto-caloric effect was first discovered, in a sense, by accident, slight irregularities being noticed in some ordinary magnetic measurements. The conclusions which have been drawn from its further study illustrate in a striking way how the careful investigation of an apparently trivial effect may sometimes lead to the most valuable results.

The work on the specific heat of ferromagnetics, and on the magneto-caloric effect, confirms Weiss's molecular-field theory in a striking manner. Essentially the orientation of particular magnetic ions in a crystal influences the orientation of all the magnetic ions in such a way that the total resultant effect is equivalent to that of a magnetic field proportional to the magnetization. The equivalence holds not only for the purely magnetic, but also for the associated thermal phenomena. The equivalent magnetic forces are much greater than those which would be exerted directly at interatomic distances if the Bohr theory presents even an approximately true picture of atomic constitution; but it has been seen (Ch. VII, sect. 3) that there is no necessity to assume that the action is direct. Indeed, the supposition seems to be definitely ruled out by the fact that much evidence, in particular that derived from the study of amorphous nickel films, indicates that ferromagnetism is essentially dependent on crystal structure. In reorientating, individual ions influence the motion of shared electrons associated with them; other ions are influenced indirectly, quantum orientation conditions probably being concerned; the crystal as a whole is distorted. The study of intrinsic and molecular fields provides no arguments definitely antagonistic to the quantum theory in general, or to its application to atomic structure in particular. There is, however, a wealth of fascinating problems awaiting further research.

In connection with Weiss's theories, the Barkhausen effect is of interest. On magnetizing a ferromagnetic material round which is wound a coil, connected through a valve amplifier to a telephone, crackling noises are heard in the telephone. These noises are the result of discontinuities in the magnetization, which can be observed directly with a galvanometer. They are associated only with the initial irreversible part of the magnetization curves, and not with the final reversible part (Forrer, 1925). The effect depends markedly on the thermal treatment the specimens have received, and so essentially on the micro-crystalline structure. For a typical specimen of iron, van der Pol estimated that there would be 6,500, and for a ferro-nickel 5,000 discontinuities per centimetre cube during magnetization. In terms of the theory, the magnitude of the discontinuities depends on the extent of the domains through which spontaneous magnetization occurs. It should be noted, however, that Tyndall, from experiments on silicon steel, has concluded that the size of the domains may be much smaller than the size of the actual crystalline "grains."

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CHAPTER XIV

MAGNETISM AND THE STRUCTURE OF THE ATOM

1. General Considerations

THE purpose of the present chapter is to survey the magnetic properties of atoms (and of ions) in relation to their general properties, as indicated by their periodic classification (Table III). The various types of experimental investigations from which conclusions may be drawn have been considered, and the results to a certain extent have been co-ordinated (Ch. X). It seems desirable, however, to review these results as a whole. Atoms or simple ions, in which the electronic configuration is influenced by a single positive charge, present the simplest problem—the magnetic properties of molecules and crystals will be briefly discussed in the next chapter—but, unfortunately, few experiments yield information from which atomic magnetic properties may be directly deduced. The susceptibilities of monatomic gases may be taken to reveal the characteristics of the atoms with reasonable certainty, but data are only available for a few of the inert gases; the Gerlach and Stern experiments give directly resolved magnetic moments of the atoms in the field direction. The ionic susceptibility measurements provide a wealth of data, but there are difficulties in interpretation, even supposing the constitution of the ions to be known. Ions in solution cannot be regarded as having the same freedom as atoms in a gas; the electronic configuration, for ions with the same number of electrons, will depend on the nuclear charge, and this is generally different for ions in solution, and for ions whose spectra may be investigated; moreover, in solution, the "normal" configuration may be considerably modified by the presence of the surrounding molecules.

For ions or atoms with the same nuclear charge and the same number of electrons, but different electronic arrangements, the name "electronic isomers" has been proposed by Swinne. The simplest illustration is provided by the hydrogen atom, with its series of possible electronic orbits. It frequently happens that the potential energy is much smaller for one of the isomers than the others, and this then constitutes the "normal state" (corresponding to the "ground-term" for the spectrum) of the atom. Thus in potassium the nineteenth electron is most firmly bound in an S orbit ($n = 4$, $k = 1$), the normal state corresponding to the (4, 1) ground-term. At a given temperature, there will be an equilibrium distribution of the different isomers, but the number corresponding to the higher quantum states will usually be small under ordinary conditions. (In the interpretation of stellar spectra, Saha's work has shown the fundamental importance of the dependence of the equilibrium distribution on temperature.) If the difference in the energy value of different possible states is small, however, an ion or atom will not have a uniquely defined electronic configuration (and consequently magnetic moment); thus, in the transition elements from Sc to Ni, the energy levels sometimes differ little, and an equilibrium distribution of different isomers may be markedly disturbed by small changes in conditions. Difficulties may then arise when the attempt is made to determine the magnetic properties to be ascribed to a definite electronic configuration.

The importance of the inert gases as standards of atomic stability, in a chemical sense, has long been recognized—an importance which has been emphasized by the quantum theory of atomic structure, in which, as already discussed, the electrons in the inert gas atoms may be regarded as constituting a "closed configuration." A new stage in the upbuilding process imagined by Bohr begins when further electrons are added to a structure of the inert gas atom type. A knowledge of the magnetic characteristics of closed configurations is essential to the understanding of the magnetic properties of atoms and ions generally; in the next section, therefore, the significance of the experimental results of the susceptibility measurements, considered in Chapter XII, will be discussed more fully, and as far as possible brought into relation with the conclusions derivable from the study of spectra.

Though the indications of the quantum theory as to the behaviour of individual electronic orbits in a magnetic field may be correct, they cannot be tested directly; in applying the theory to atoms generally, the mutual influence of different electronic orbits must be taken into account, and the manner in which the quantum conditions should be formulated is by no means clear. The difficulties appear most prominently in connection with the interpretation of the multiplet structure of spectra, which has already been discussed in some detail.

Possible resolved magnetic moments for an atom in a definite spectral state are given by the corresponding *mg* values (Table XXVII), and in so far as the theoretical *mg* values lead to results in agreement with experiment, as they do for a great number of spectra, analysis of the spectra yields very precise information as to the magnetic properties of the atom. The magnetic-moment possibilities vary with the spectral state; but the "normal" magnetic state may be deduced when the "ground-term" is known. A specification of the multiplicities of the spectra to which an atom gives rise, and of the spectroscopic ground-term, provides, then, a concise summary of the atomic magnetic properties also, and for the present purpose that is what is required.

An example may make the procedure clear. Suppose that analysis of the spectra has shown that the ground-term is one corresponding to $k = 3$ in a triplet series (a ^3D term). Inspection of Table XXVII shows at once what are possible resolved magnetic moments for the atom, and in particular that the maximum value is 4. There are, however, three ^3D states, corresponding to $j = 1$, 2 and 3; and the magnetic properties of the atom are not precisely determined unless the j value of the atom in its normal state is also known—that is, whether it corresponds to $^3D_1$, $^3D_2$ or $^3D_3$. If the normal state was known to be $^3D_1$, then it could be predicted that in the magnetic deviation experiments traces corresponding to $\mu = \pm \frac{1}{2}$ and 0 would be found; and the susceptibility of the monatomic gas could be calculated. It is frequently possible to determine the $^r k$ state corresponding to the normal atom when the particular $^r k_j$ state is uncertain. If the energies of the j components are not widely different, then there may be an equilibrium distribution of atoms in different j states; this may give rise to some of the apparent anomalies encountered in connection with ionic moments.

The physical interpretation of the significance of the spectral characteristics generally in relation to the structure of the atom is a wider problem, whose difficulties have been emphasized; a more detailed discussion than that which has already been given hardly falls within the scope of the present book, particularly as a survey within reasonable limits of space is almost impossible, partly owing to the amazingly rapid development of the experimental side of the subject, but still more owing to the uncertain and ever-changing character of the theoretical outlook. Only a few of the more salient points which have emerged from recent work can be mentioned, and an indication given of the lines along which the problems are being attacked.

It has been known for some time that in a spectrum such as the triplet spectrum of Ca, in addition to the ordinary terms (e.g. p terms), there are other terms, symbolized by dashes (e.g. p' terms), which behave similarly as regards Zeeman separations, but have different combining properties. Among themselves ordinary and dashed terms both combine in accordance with the usual azimuthal quantum number selection rules ($\triangle k = \pm 1$)—thus pd and $p'd'$ combinations occur. In addition, there are intercombinations, giving strong lines, of the pp' and dd' type, apparently corresponding to $\triangle k = 0$. (There are also intercombinations apparently corresponding to $\triangle k = 2$.) A comprehensive investigation by Russell and Saunders has shown that in the alkaline earth spectra the dashed terms are comparable in importance to the familiar terms. A consideration of the energy values of the terms provides practically conclusive evidence that intercombinations of the pp' type correspond to simultaneous transitions of two electrons (the frequency being determined by the *total* energy change). Millikan has accounted for characteristic groups of lines in two and three valence atomic systems in a similar manner. This at once suggests the direction in which a more complete analysis of spectra must be sought. In a typical alkali metal atom, such as sodium, giving a doublet spectrum, there is one electron (the valence electron, in Na in a (3, 1) orbit) much more loosely bound than the others constituting the inert gas-like core. When the excitation conditions are not too powerful, the quantum orbit of this " outer " electron only will be affected; and the spectral terms can be expressed by quantum numbers characterizing the possible orbits of this one electron. When there are a number of electrons moving in orbits such that relatively small amounts of energy are sufficient to bring about transitions, remembering that the spectral line frequency is determined by the total energy change, it will follow that the quantum numbers which are appropriate for the specification of the spectral terms will be characteristic not of a single series electron, but of a number of electrons considered together. An application of this conception to the interpretation of complicated spectra has been made by Hund, who bases his treatment on a formal scheme put forward by Heisenberg.

For hydrogen there is one term corresponding to a given value of k for the electron; in ordinary one-valence electron systems, however, there are, in general, two different terms corresponding to a single k (e.g. p_1 and p_2 in sodium). This term-splitting arises owing to the interaction of the series electron with the inert gas core, and this may be regarded alternatively as due to an apparent doubling of the number of possible stationary states of the electron (as in the "relativity" explanation) or from a doubling of the number of possible stationary states of the core (as in the "magnetic" explanation). Accepting the doubling as a fundamental empirical fact, however, and without inquiring into its precise physical significance, it is possible to build up a scheme, with quantum numbers to specify the terms, giving a complete formal descriptive analysis of the observed series types and multiplicities for systems with one or more valence electrons. The comprehensiveness of Heisenberg's scheme undoubtedly marks a great advance, but a number of points of physical interest tend to be obscured—it is sometimes forgotten that a descriptive scheme is not an end in itself. One of the main features of the scheme, however, has a definite physical significance. When there may be more than one electron concerned in the transitions giving rise to the spectral lines, the stationary states are more appropriately specified by a quantum number l, which is of the nature of a vector sum of the k's of the individual electrons. It is actually l and not k which should enter into Landé's expression for the splitting factor g (equation 10, Ch. X). Now in the spectra from K–Ni, terms have been classified mainly by their behaviour in the Zeeman effect; with the present outlook it follows that the k's so assigned are not necessarily characteristic of an individual "series" electron, but are really l's characteristic of a group of electrons. Hund's development of these ideas has cleared up a number of outstanding anomalies. Thus, in the spectra of Ti and V, the ground-terms have been classified as F terms, which, on the older view, would correspond to a series electron moving in an orbit for which $k = 5$. From the general quantum theory of atomic structure (Ch. V) it would appear that the last bound electrons should be in (3, 3) orbits ($n = 3$, $k = 3$). Hund, however, finds that a triplet F term (as observed for Ti) is the ground-term to be anticipated if, in addition to the electrons in the completed argon configuration, there are 2 electrons in (3, 3) and 2 in (4, 1) orbits; and a quartet F term (as for V) for 3 electrons in (3, 3) and 2 in (4, 1) orbits. An essentially important point which emerges is that the types of spectra generally, and the ground-terms in particular, are in complete accordance with what may be anticipated from an upbuilding of atoms according to the modified Bohr scheme, sufficiently if summarily indicated in Table V.

Hund has further applied the Heisenberg principles to a consideration of the ionic magnetic properties of the rare earths (see Table XXI and Fig. 31). On the whole good agreement is obtained, but some of the assumptions involved are rather uncertain. In the K–Cu group the agreement is not satisfactory. There are still many problems in ionic magnetism awaiting further investigation.

In the present state of flux of theory, further discussion of the multiplet structure of spectra would be out of place in a book primarily on magnetism ; but it is hoped that some idea has been conveyed as to the general lines along which work is progressing. The artificial and formal nature of many of the schemes that have been proposed is recognized by the authors of them, and it cannot be over-emphasized that the schemes should be looked on simply as stepping-stones towards a more satisfactory physical explanation of the experimental facts. There is ample scope for much further work. In this is required the clear vision of the sincere scientific artist, who can see, and render visible, an order underlying the apparent chaos ; and who, from the wealth of materials, can build up a design which is harmonious and intellectually satisfying.

2. The Inert Gases. Closed Configurations

The inert gas atoms have completed electronic configurations, and the supposition that the orbits balance magnetically is the natural straightforward interpretation of the observed fact that the gases are diamagnetic. Before considering the significance of this, it is desirable to examine as precisely as possible how far the values for the mean square radius of the electronic orbits deduced from the atomic susceptibilities is in agreement with the values deduced from other evidence. The calculations of Chapter XII have shown that the values are at least of a reasonable order of magnitude ; these calculations can to a certain extent be refined in a manner which has been suggested by Joos. The probable electronic constitutions of the inert gas atoms are shown in Table V. From XII (1) and (1.1), if $\overline{r^2}$ is the mean square radius of an electronic orbit, assuming random orientation

$$\chi_{At} = -\frac{e^2}{6mc^2}\sum_{N}\overline{r^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Multiplying by Avogadro's number, this gives for the gram-atomic susceptibility

$$\chi_{A} = -2{\cdot}85 \times 10^{10}\sum_{N}\overline{r^2} \quad . \quad . \quad . \quad . \quad . \quad (1.1)$$

For orbits characterized by the same quantum numbers

$$\overline{r^2} \propto \frac{1}{Z_{\text{eff}}^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where Z_{eff} is the effective nuclear charge.

In neon the contribution of the two inner electrons to the susceptibility will be roughly $\left(\frac{2}{10}\right)^2$ that of the atomic susceptibility of helium, and so will be negligible (see Table XXXVI). From XII (4.1)

$$N\overline{r^2} = -[\cdot 351\chi_A \times 10^6] \times 10^{-16} \quad . \quad . \quad . \quad . \quad (3)$$

The value of $\sqrt{\overline{r^2}}$, which may be deduced from (3) by inserting the observed value of χ_A for neon $(6{\cdot}1 \times 10^{-6})$ and putting $N = 8$, should therefore be comparable—since only the outer electrons moving in orbits for which $n = 2$ are involved—with the somewhat indefinite "radius of the atom." The value obtained is $\sqrt{\overline{r^2}} = {\cdot}52 \times 10^{-8}$. In a similar way the effect of the neon core in the argon atom may be allowed for; and this leads to a value for the mean radius of the outer electron orbits (the M electrons, in $n = 3$ orbits) lying between ·81 and ·86 A.U. These results may be compared with those deduced by extrapolation from the radii of combination of ions in crystals by Bragg, and by Fajans and Herzfeld (as quoted by Joos); and those deduced from the mean collision area, calculated from the viscosity of gases, by Rankine.

	Diamagnetism.	Crystals.		Viscosity.
		B.	F. and H.	
Ne . .	·52	·65	$\cdot 63 < r < \cdot 75$	1·17
A . .	·84	1·02	$\cdot 79 < r < \cdot 95$	1·43

TABLE XXXVIII.—MEAN "ATOMIC RADII" (IN A.U.).

In view of the indefiniteness of the term "atomic radius," the interpretation of which differs according to the class of phenomena considered, the general agreement as to order of magnitude is sufficiently satisfactory to justify the conclusion that the usual theory of atomic diamagnetism is, in its main lines, correct.

An estimate of the dimensions of electronic orbits may also be obtained from spectroscopic data, and although only rough calculations can be made, it may be of interest to give some of them, for it seems possible that refinements, in the light of future investigation, may lead to conclusions of considerable importance. From the equations of Chapter V (18–21) it may readily be deduced that the mean square radius of a hydrogen-like (n, k) orbit, the effective nuclear charge being Z, is given by

$$\overline{r^2} = \frac{hk}{4\pi^2 m} \times \frac{1}{2\mathrm{R}c} \times \frac{n^3}{\mathrm{Z}^2} \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

$$= kn\left(\frac{n}{\mathrm{Z}}\right)^2 a_{\mathrm{H}}^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4.1)$$

where $a_{\mathrm{H}} = \cdot 532 \times 10^{-8}$ cm.

$$\overline{r^2} = \cdot 283 \times 10^{-16}\ kn\left(\frac{n}{\mathrm{Z}}\right)^2 \quad . \quad . \quad . \quad . \quad . \qquad (4.2)$$

This gives, from (1.1) for the mean diamagnetic susceptibility associated with (n, k) orbits orientated at random,

$$\chi_{(n,\,k)} = -\cdot 81 \times 10^{-6}\,\frac{kn^3}{\mathrm{Z}^2} \quad . \quad . \quad . \quad . \quad . \qquad (4.3)$$

A rough estimate of the effective value of $\left(\frac{n}{\mathrm{Z}}\right)$ may be obtained if the energy of the corresponding (n, k) term in the atom is known. For the present purpose, however, it will be more convenient, in that only outer electrons will be taken into account, to express relations for these in terms of the ionizing potential of the atom. Let I be the ionizing potential, expressed in volts, of the atom considered, $\mathrm{I_H}$ that of the hydrogen atom, with the electron in a (1, 1) orbit. ($\mathrm{I_H} = 13 \cdot 5$.) By an application of V (13)

$$\mathrm{I} = \left(\frac{\mathrm{Z}}{n}\right)^2 \mathrm{I_H} = 13\cdot 5\left(\frac{\mathrm{Z}}{n}\right)^2 \quad . \quad . \quad . \quad . \qquad (5)$$

Substituting in (4.2), for the mean square radius of the outer (n, k) electron orbits

$$\overline{r^2} = \cdot 283 \times 10^{-16} \times 13\cdot 5\,\frac{kn}{\mathrm{I}}$$

$$= kn\,\frac{3\cdot 83}{\mathrm{I}} \times 10^{-16} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

For neon the ionizing potential—corresponding to removal of a (2, 2) electron—is 21·5 ; for argon—(3, 2) electron—15·3.

$$\left.\begin{array}{llll} \text{Ne} & \overline{r^2_{(2,2)}} = \cdot 712 \times 10^{-16} & \text{A} & \overline{r^2_{(3,2)}} = 1\cdot 5 \times 10^{-16} \\ & \sqrt{\overline{r^2_{(2,2)}}} = \cdot 84 \text{ A.U.} & & \sqrt{\overline{r^2_{(3,2)}}} = 1\cdot 2 \text{ A.U.} \end{array}\right\} \qquad (7)$$

Though there is again agreement as to order of magnitude, inspection of Table XXXVIII shows that the values are high compared with those deduced from the susceptibility. Too much significance should not be attached to this, owing to the crude character of the calculations. (An effective value of n, as well as of Z, should probably be taken.) It may be noted, however, that the discrepancy becomes very marked if the atomic susceptibilities are calculated from the mean square radii deduced from the ionizing potential. For Ne, with two (2, 1) electrons (orbital area half that of the 2, 2) and six (2, 2); and for A, with two (3, 1) and six (3, 2), from (1.1) and (7)

χ_A calc. Ne $14{\cdot}3 \times 10^{-6}$ A 30×10^{-6}

These are greatly in excess of the observed values

χ_A obs. Ne $6{\cdot}1 \times 10^{-6}$ A $16{\cdot}5 \times 10^{-6}$

In the deduction (1) it is assumed that the orbits are orientated at random. Now the Zeeman-effect observations would suggest that inert gas atoms, in common with all closed configurations possessing zero moment, orientate themselves in one definite direction with respect to the field; if the atoms set themselves so that the mean projected value of $\overline{r^2}$ at right angles to the field is as small as possible (in other words, so that the planes of the orbits in the atom are, as far as possible, at right angles to the field), then the calculated susceptibility would be smaller by a factor of the order of, but not less than $\frac{2}{3}$ (cf. XII, 6.3), so bringing them into closer agreement with observations. More refined calculations may enable more light to be thrown on this complicated orientation question.

Helium has not so far been discussed, partly because of the greater uncertainty of the relevant ionic and crystal data; and partly because it is improbable that the magnetic measurements have the same degree of accuracy as those for neon and argon, owing to the low volume susceptibility and other difficulties. The importance of the "helium problem," however, justifies a brief consideration of the nature of the contributions towards its solution which may be made from the magnetic side. The ionizing potential of helium is 24·5 volts, and assuming that the two electrons normally move in (1, 1) orbits, the mean square radius may be calculated as above from (6). (Z, the effective positive charge, comes out as 1·35.) The "diamagnetic value" may be calculated, using (3), from Wills and Hector's result for the gram-atomic susceptibility—$\chi = 1{\cdot}7 \times 10^{-6}$ (Table XXXVI).

		$\overline{r^2}$.	$\sqrt{\overline{r^2}}$.
He	From I.P.	$\cdot 156 \times 10^{-16}$	·394 A.U.
	From χ	$\cdot 30 \times 10^{-16}$	·55 A.U.

20

The ionizing potential leads to a considerably smaller value for the radius than the susceptibility, the results contrasting with those for neon and argon. The susceptibility which the spectroscopic radius would indicate from (1.1) for random orientation of orbits is $\cdot 90 \times 10^{-6}$; as a maximum, with all the orbits at right angles to the field, $1\cdot 35 \times 10^{-6}$, a value 20 per cent. lower than that observed. It seems unlikely, but not impossible, that the experimental difficulties may be responsible for the discrepancy, and further confirmatory susceptibility measurements are obviously desirable. It should be noted that comparison has been made with orbital magnitudes deduced from actual experimental spectroscopic data; not with those of "model" helium atoms. The magnetic properties of some of these "models" will now be discussed.

The configuration of the electrons in the normal helium atom is presumably similar to that of the K group in atoms generally containing more than two electrons, so that the helium problem has a wide bearing. General evidence indicates that the configuration should have a high degree of symmetry, and that the two electrons should be moving in similar orbits. As the earlier simpler models failed to give satisfactory values for the ionizing potential, or were ruled out owing to their probable instability, or on other grounds, the Bohr-Kemble crossed orbit model, whose properties have been investigated in great detail by van Vleck and Kramers, has generally been considered the closest approximation to the true picture. It may be said at once, however, that its provisional acceptance has been due rather to the lack of anything better than to its own inherent satisfactoriness. In this model, the electrons are assumed to rotate in circular (1, 1) orbits, the normals to the orbits being inclined at 120°. The atom as a whole will then have unit resultant magnetic and mechanical moment, measured in Bohr units. The rather disappointing result of long and laborious computation is that the ionizing potential would be 20·7 volts, while the observed value is 24·5. This might be due to inappropriate formulation of quantum conditions, or to the interaction of the electrons not being describable in terms of the simple laws of force assumed to hold. That the model has a magnetic moment would seem a fatal objection in view of the diamagnetism of helium. This has been met by the subsidiary hypothesis that the atom invariably sets itself with its moment at right angles to the field direction. While it is almost certainly true that there is only one stationary orientation for the atom in a field, the view that the atom has unit moment seems curiously artificial; for atoms which definitely have unit magnetic moment (as Cu, Ag, and Au in the Gerlach and Stern experiments) do behave, in respect to orientation, in accordance with the straightforward quantum theory indications. The mutual energy associated with valence electron orbits and the K layer in atoms generally would vary with the orientation—this forming the basis of the older magnetic explanation of multiplets. In a single family of elements, as the atoms increase in atomic number, the ratio of the mechanical to the magnetic moment of the K electrons (assuming the pair to have the crossed-orbit configuration) should also increase, owing to the relativity change in mass. As the mechanical moment would remain constant, the magnetic moment would decrease. Pauli has shown that this would lead to irregularities in the observed Zeeman separations, well within the range of detection, but of which there is no experimental indication. He concludes that the mechanical (and magnetic) moment of the K " shell " is zero, and that, in this respect, it is similar to closed configurations of the inert gas type generally.

As to orbital dimensions, the model would lead to susceptibility values much the same as those deduced from the ionizing potential. On the whole it may be concluded that the model is not satisfactory. Whatever the difficulties may be in the way of precise formulation, by far the simplest and most satisfactory crude model is one in which the two electrons rotate in opposite directions in similar (n, k) orbits so that the resultant moment vanishes. It is obvious that a description of the same circular orbit in opposite directions round the nucleus is impossible, and to evade this difficulty Sommerfeld, in the fourth edition of *Atombau*, has proposed a model in which an azimuthal quantum number 1 is assigned to the two electrons together, but to each separately $\frac{1}{2}$; the electrons are supposed to move in opposite directions in co-planar elliptical orbits ($n = 1$, $k = \frac{1}{2}$), such that their major axes are in line, and the aphelia on opposite sides of the nucleus. Preliminary calculations indicate an ionizing potential of the right order, but the model is probably unstable. For the major and minor axes, in terms of the radius a_H of the hydrogen (1, 1) orbit, approximately, $a = \frac{a_H}{2}$; $b = \frac{a_H}{4}$. From this it may readily be calculated from (4.1) and (4.3) that $\chi_A = \cdot 20 \times 10^{-6}$ (a maximum value would be $\cdot 30 \times 10^{-6}$). This is much below the observed value, and suggests that the orbital areas of the model are too small.

It seems not impossible that the electrons are both moving in circular (1, 1) orbits, in opposite directions, the orbits being parallel, and their planes not passing through the nucleus

Such a model would have zero moment, and a high symmetry, and its ionizing potential would be somewhat the same as the crossed-orbit model, though its stability might be doubtful. It should be noted, however, that the electron in each orbit would be in a possible stationary state, as regards orientation, in the field of the other. Hitherto the most fruitful atomic models have been those in which the planes of the electronic orbits pass through the nucleus, but this is probably simply because their mathematical treatment is not quite so far beyond the bounds of possibility; the chemical evidence seems to favour a spatial distribution of orbits of a more thoroughgoing character than that usually considered.

As to the orientation of the parallel-orbit model in a field, although there is only one setting, it is uncertain how the planes of the orbits set themselves in the field. (The setting of the two valence electron orbits in singlet atoms in the S state is also uncertain.) Here the Glaser experiments may be recalled; the question arises as to whether or no the apparent diamagnetic susceptibility of the inert gases will be found to be a function of the field and pressure; the significance, in connection with orientation, is obvious.

Summarizing, for the inert gases generally the actual measured susceptibilities are in fair agreement with theoretical indications, but there are discrepancies to be cleared up. It may be concluded that the atoms have zero mechanical and magnetic moment, a characteristic which they have in common with atoms or ions possessing completed configurations.

A configuration may be regarded as closed when all the subgroups, characterized by a definite azimuthal quantum number k, have their full complement of electrons (see Table V). This is possible with the numbers of electrons in the inert gas atoms; and for these the closed configuration is also the most stable when the nuclear charge is equal to the number of electrons. There are, however, other numbers of electrons than 2, 10, 18, 36, 54 and 86 which are capable of building up closed configurations; thus 28 electrons may fill the K, L and M levels completely, though this does not correspond to the most stable grouping when the nuclear charge is 28 in nickel. (Oseen has, however, suggested that in the non-magnetic nickel films the atoms may be in this electron-isomeric state.) In a similar way, as may readily be seen from Table V and III, 46, 68 and 78 electrons can also form completed structures, and in this connection it is interesting to note that the elements Ni (28), Pd (46), Er (68) and Pt (78) are chemically considered as "sub-standards of atomic stability" in theories of the Langmuir type. If two electrons moving in orbits for which $k = 1$, and for which n is the same, are added to a closed configuration, a further closed configuration may be formed, as in Be, Mg, Ca, etc., Zn, Ca, Hg, when these are in the ^1S state corresponding to the singlet spectrum.

Closed configurations may be regarded as starting-points for analogous processes of upbuilding as successive electrons are added; it is the resulting sequential and "family" magnetic relationships which will be discussed in the next section.

3. Sequential and Family Relationships

In considering the properties of the elements, as classified in a periodic scheme, it is of interest to compare successive elements forming a sequence (those in the rows in the usual form of the table, and in the vertical columns of Table III), and also analogous elements of a family (in vertical columns in the usual table, and joined by lines in Table III). Sequential relations have already been discussed in connection with the magnetic and spectroscopic characteristics of the elements from potassium to copper (see Fig. 42, and Table XXVIII, Ch. X), and the magnetic characteristics of the ions of the rare earths (see Table XXI and Fig. 31, Ch. VII). Attention will now be mainly directed to family relationships; consideration of these, together with the sequential relationships, will enable a broad general view of the atomic magnetic properties of the elements as a whole to be obtained.

The atoms to be considered first are those immediately succeeding the inert gases, or the "sub-standards of atomic stability," Ni (28), Pd (46) and Pt (78); so containing one electron in addition to those in closed or potentially closed configurations. These are shown in the following scheme, taken from Table III.

(1 H) —— 3 Li —— 11 Na —— 19 K —— 37 Rb —— 55 Cs —— 87 —
\ 29 Cu —— 47 Ag —— 79 Au

In each of these atoms, in its normal state, according to the Bohr scheme, there is one electron moving in an orbit of unit azimuthal quantum number, this electron being the first of a new group. (Thus, in K and Cu, the additional electron is the first in the N level, and moves in an orbit for which $n = 4$, $k = 1$. Between K and Cu, the underlying M levels have been filled up.) It would be anticipated that the atoms would have unit magnetic moment; in complete accordance with this, in the Gerlach and Stern experiments, the resolved moment of Cu, Ag and Au atoms is found to be one Bohr magneton, the atoms presumably setting themselves so that the plane of the orbit is at right angles to the field, the moment being parallel to the field—in the same or the opposite direction. The other atoms would undoubtedly behave similarly. In this connection it is of interest to note that Taylor and Lewis have found that a solution of sodium in liquid ammonia is paramagnetic. (Details of the measurements are not yet available.) All the atoms give doublet spectra, and have a ^2S ground-term. (It will be convenient, in this section, to adopt the notation suggested by Russell and Saunders, in which the multiplicity is denoted by an index at the upper left hand, and the series by a Roman capital, whatever the multiplicity. S, P, D, F, G . . . have their usual significance, corresponding, in the simpler types of spectra, to $k = 1, 2, 3$ . . .) The spark spectra of these elements are all complicated, as would be anticipated. The arc spectra, corresponding to the unionized atoms, are simple for the Li–Cs series, but Cu, Ag, and Au all give complex spectra, rich in lines. This must be traced to the fact that the valence electron is not so sharply differentiated as regards its energy from those in the core, so that, although a configuration in which all but the last of the electrons form a closed group is a possible one, other electron-isomeric states are possible, to each of which will correspond characteristic spectra.

Hydrogen is in a class by itself, for the "core" consists simply of a proton. The fine-structure of the lines does not correspond to a multiplicity of the terms in the usual sense, but arises from the difference in the relativity effect for orbits of different types. The main fine-structure components of the Hα line, for example, correspond to the transitions $3D \longrightarrow 2P$, $3P \longrightarrow 2S$, and the weak satellite to $3S \longrightarrow 2P$. That the general relativity formula which gives, for example, the separation between 2P and 2S (circular (2, 2) and elliptical (2, 1) orbits) also serves to give approximately multiplet separations of the ordinary type, such as that between $2P_1$ and $2P_2$ for lithium, is a difficulty which has already been discussed (Ch. X, sects. 5 and 6). The fact that observations can be correlated by assuming the terms in hydrogen to be simple, however, points clearly to the view that doublets arise from interaction between a valence electron and electrons in a completed core, and multiplets generally from interaction between electrons; in other words, that multiplet structure is primarily of magnetic origin, in spite of the fact that slight manipulations of the relativistic formula enable it to cover observed separations.

The atoms of the next series of elements contain two "additional" electrons:

$$\begin{tikzcd}
4\ \mathrm{Be} \arrow[r, dash] & 12\ \mathrm{Mg} \arrow[r, dash] \arrow[dr, dash] & 20\ \mathrm{Ca} \arrow[r, dash] & 38\ \mathrm{Sr} \arrow[r, dash] & 56\ \mathrm{Ba} \arrow[r, dash] & 88\ \mathrm{Ra} \\
 & & 30\ \mathrm{Zn} \arrow[r, dash] & 48\ \mathrm{Cd} \arrow[r, dash] & 80\ \mathrm{Hg} &
\end{tikzcd}$$

A closed configuration may be formed if the two electrons move in S ($k = 1$) orbits in opposite directions; the atoms will then possess zero magnetic moment. This seems to be the normal state. In the magnetic deviation experiments, no deflection is found for Zn, Cd and Hg; and mercury vapour is diamagnetic. The Ra arc spectrum has not been analysed, but all the other elements give singlets and triplets, with a ^1S ground-term, corresponding to zero resolved magnetic moment for the atom (see Table XXVII). The ^3S terms probably correspond to both the electrons rotating in the same direction. It seems to be a general rule (to which the modified Bohr scheme of Ch. V conforms) that there cannot be more than one electron in an atom moving in an orbit characterized by exactly the same quantum numbers (n, k, j and m) as has been pointed out by Pauli; and he notes, in connection with this, that the lowest triplet S term corresponds to a value of n greater by 1 than the lowest singlet S term (in which m is different for the two electrons, corresponding to their opposite rotation). Although the normal state of the atoms corresponds to atomic diamagnetism, this is not necessarily the only possible state (the triplet S term, for example, would correspond to resolved moments of ± 2 as well as 0). This may form the basis for an explanation of the "residual paramagnetism" observed in some of the solid elements (e.g. Mg, Ca, Ba—Table XIII). The spark spectra of the singly ionized atoms uniformly show doublets.

Helium, with its two electrons, must be placed in a category of its own. It is the only atom which gives series of odd and even multiplicity—singlets and doublets. The doublets, however, are certainly not of the usual type, the intensity ratio of the components corresponding to the $p \longrightarrow s$ transition, being approximately 6 to 1 and in the inverse order to that of the typical alkali metal doublets, with an intensity ratio of 2 to 1. Whether the doublets are "real" doublets is uncertain, but intercombinations between the doublet and singlet terms do not normally occur, which indicates that the doublets do not correspond to the triplets of the ordinary two-electron systems. When a second electron is added to a typical one-valence electron system (as in passing from Na to Mg), the doublets "branch" into singlets and triplets. It would appear that a singlet-triplet system is only characteristic of two "additional" electrons when the first, by its interaction with a completed core, can give rise to doublets. Ionized helium gives a singlet system. A second electron might be expected to give a doublet system, in accordance with a branching rule, though this removes no difficulties. It is clear, however, that it is the presence of a completed core in a typical alkaline-earth atom which is responsible for the difference between its spectral behaviour and that of helium. The attribution of the singlet series to the crossed-orbit atom, and the doublet to the coplanar-orbit atom, does not lead far, particularly as the evidence discussed in the last section makes the crossed-orbit model very doubtful.

Two electrons moving in $k = 1$ orbits are capable of forming a completed configuration, and when there are no underlying levels to be filled up, it would be anticipated, in accordance with the scheme of Table V, that the next electron would enter a $k = 2$ orbit, so beginning the subgroup II of the L, M, N . . . levels, in the following elements:

5 B —— 13 Al —— 31 Ga —— 49 In —— 81 Tl

The atoms all give doublet spectra, having ^2P ground-terms. (It is noteworthy that quartet terms have not been found, fitting in with the rules of Ch. X, from which it follows that the maximum multiplicity is one greater than the number of electrons external to a closed configuration.) Thallium, with a magnetic deviation corresponding to $\mu = \pm \frac{1}{3}$, behaves in agreement with the Zeeman-effect *mg* values for a $^2P_1$ term (Table XXVII). Dissolved in mercury, correspondingly, Tl has been found to be paramagnetic by Taylor and Lewis. It may then be supposed to be in its normal atomic state; as a solid, however, Tl is diamagnetic as are all the other elements, except Al, which shows strong residual paramagnetism. In accordance with the alternation rules singly and doubly ionized Al (Al II and Al III) give singlet-triplet and doublet spectra respectively.

Silicon has been most investigated spectroscopically in the next series, particularly in regard to its spectra at successive stages of ionization (Paschen, Fowler). The alternation rules are illustrated in a most striking manner.

6 C —— 14 Si —— 32 Ge —— 50 Sn —— 82 Pb

SiI gives triplets, and has a $^3P_0$ ground-term, corresponding to zero resolved magnetic moment. Sn and Pb atoms are undeflected in the deviation experiments, indicating that for them also, in the normal state, the resolved moment is zero. The spectra have been partially analysed (Sponer). Triplets definitely occur for Pb, and are probable for Sn. The lowermost terms in Sn and Pb appear to be P terms, with *j* values 0, 1, 2, 2, 0; these *j* values fit in with the Pauli-Heisenberg schemes; and the $j = 0$ value corresponds to the normal zero moment state. Singly ionized C and Si give doublets, and have ^2P ground-terms.

Little can be said about the $2 + 3$ electron atoms:

7 N —— 15 P —— 33 As —— 51 Sb —— 83 Bi

As there are odd numbers of electrons even multiplicities would be anticipated. Doublets are found for P; and for N, which has a ^2P ground-term, there are doublets and quartets (Kiess). A zero magnetic moment would not occur for ^2P ground-terms (though it is possible for ^4D terms—see Table XXVII), and the non-deviation of Sb rays, and the unilateral deviation of Bi rays, is surprising; but, as pointed out in the discussion of the Gerlach and Stern work, the proportion of molecules is high with these elements.

The next series, normally with four electrons in $k = 2$ orbits, and so lacking two of the complete group of six, are reciprocal, in the Pauli sense (Ch. V, sect. 2), to those which have only two (the C–Pb series):

8 O —— 16 S —— 34 Se —— 52 Te —— 84 Po

There are analogies, for O, S and probably Se give triplets. Quintets also occur for S and Se, and probably for O. O and S have ^3P ground-terms. There is no direct evidence as to the atomic magnetic properties, though the Landé *mg* table would indicate a normal moment of 3 for O.

The spectra of the halogen atoms—

9 F —— 17 Cl —— 35 Br —— 53 I —— 85—

have not been analysed. The electronic configuration will be reciprocal to those of atoms of the Al type, having one electron less than is required for a completed group. Doublets may be anticipated in the spectra (Cl II gives uneven multiplicities) and the free atoms, in their normal state, would have a magnetic moment.

The transition elements are of two types, according as IV and V underlying sub-levels (corresponding to $k = 3$) are being filled up, as in the sequences ending with Ni, Pd and Pt, or the VI and VII sub-levels ($k = 4$) as in the rare earths. The families may conveniently be considered in relation to the sequences:

21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni
39 Y	40 Zr	41 Nb	42 Mo	43 Ma	44 Ru	45 Rh	46 Pd
71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt
89 ——	90 Th	91 UX	92 U				

The first transition series are built up on the argon configuration with 2K, 8L and 8M electrons (of the M electrons—for which $n = 3$—2 are in subgroup I, with $k = 1$, and $2 + 4$ in subgroups II and III, with $k = 2$). The 19th electron in K and Ca$^+$ is bound in a (4, 1) orbit; but in Sc^{++} in a (3, 3) orbit. Sc in its normal spectral ground-term state probably has 2 (4, 1) electrons and 1 (3, 3) electron, and according to Hund's treatment, the Sc–Ni spectra are consistent with normal configurations in which there are 2 (4, 1) electrons (in the N I sub-level) and 1 to 8 (3, 3) electrons (in the M IV and V levels) (see Table V). Cr is probably an exception, having only 1 (4, 1) electron. The spark spectra indicate that the singly ionized atoms normally have 1 (4, 1) electron. The spectral characteristics are summarized in Table XXVIII, to which may be added for Co $r = 2, 4, 6$ (^{4}F ground-term) (Walters, Catalan and Bechert) and for Ni $r = 1, 3, 5$ (^{3}F ground-term) (Bechert and Sommer). The magnetic characteristics of the ions are given in Table XX, and while, as has been stated above, these may be brought into relation with the spectra, the correlation is at present far from complete. In the magnetic-deviation experiments, the presence of undeflected traces for Fe and Ni is consistent with the uneven multiplicities of their spectra; unless, however, $j = 0$ for the normal atom, deflected traces should be present as well. These are found for Ni. Though there is no necessity to suppose that there is any fundamental anomaly, complete correlation is again lacking, and until further experimental work is carried out, only a speculative discussion could be given.

With respect to the family relationships, it may be said that as far as investigation has gone, analogous elements give similar spectra. As an example, Mo, like chromium, gives septets, quintets and probably triplets, and septets have also been found in the W spectrum; Ru gives quintets, having a ^{5}D ground-term like Fe. The spectral similarity indicates similarity in the electronic configurations, and though the starting-points in particular upbuilding processes may be uncertain, the three sequences of elements and the fourth partial sequence may be taken to correspond generally to the filling up of the underlying M, N, O and P IV and V sub-levels respectively. Practically no ionic susceptibility measurements seem to have been made for any except the first of these transition-element sequences. The desirability of such investigations need hardly be emphasized. With respect to similarity in magnetic behaviour, it is of interest to recall that Ni (above the Curie-point), Pd and Pt form paramagnetic solids (the metal crystals are all face-centred cubic) whose susceptibility temperature curves all lead to a Weiss magneton value of about 8 or 9 (cf. Ch. VII, sect. 2).

Though there are some analogies between the Al–Cl (or the Be–F) and the Sc–Mn elements, there are characteristic differences: in chemical behaviour, because in the transition elements of the group which is being built up is an underlying one; and in spectroscopic behaviour, because it is a $k = 3$ group (requiring a total of 10 electrons for completion) and not a $k = 2$ group (requiring 6). Higher multiplicities are found in the transition-element spectra than in the spectra of the elements of the short periods.

The subdivision of the $k = 3$ electrons into two subgroups, with 4 and 6 electrons, does not show itself in the sequential development either of the magnetic or spectral properties. This, however, is not surprising, for the particular subdivision is appropriate only to the closed configurations.

Up to the present, little progress has been made in the analysis of the rare-earth spectra. The magnetic properties of the ions have been sufficiently considered (Ch. VII, Table XXI), and the deductions as to spectral multiplicities which may be made have been discussed (Ch. X, sect. 4). In Hund's treatment of the question of the ionic moments, the probable ground-terms of the ions are arrived at by applying Heisenberg's principles. Thus, for Ce^{+++}, a ^2F ground-term is found. A somewhat uncertain empirical rule is then used to determine which of the possible j components of the ^2F term corresponds to the normal state of the ion, and the Weiss magneton value calculated for this in the usual way. Good agreement with the experimental values is obtained, but the problem is far from closed. On the basis of the electronic configurations deduced for the ions, Hund suggests a probable distribution of electrons in the normal atoms. From La (57) to Lu (71) the atoms probably have 2 (6, 1) electrons and 1 (5, 3) electron (Lu being analogous to Sc, as above), while the number of (4, 4) electrons increases from 0 in La to 14 in Lu.

The survey of the periodic table shows that the magnetic properties of atoms, so far as they are known, fall into line with the chemical and spectroscopic properties, being generally capable of correlation in terms of the general quantum theory of atomic structure. There are wide fields for future experimental investigation; the theories are deficient and inadequate; but, in emphasizing the fact that there are many unsolved problems, the remarkable achievement of the quantum theory should not be forgotten. In the course of but a few years, the new outlook has enabled an extensive series of apparently disconnected phenomena to be correlated and interpreted, and as a result of the clear conception which has been obtained of the essential significance of atomic magnetism, the special study of the magnetic properties of atoms will be able to contribute more and more towards the solution of the problems of atomic structure generally.

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PAULI, *Zeit. f. Phys.* 31, 373 (1925) (see Ch. X), and for ionic diamagnetism, Joos's papers (*l.c.* Ch. XII). (2)

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KAYSER. *Handbuch der Spektroskopie*, 6 Vols. Vol. 7 in preparation. (Leipzig.)

FOWLER. *Report on Series in Line Spectra*, London Phys. Soc. (1922).

PASCHEN und GÖTZE. *Seriengesetze der Linienspektren* (Berlin, 1922).

The more recent work is extensively cited by Sommerfeld (*Atombau*) and Back and Landé (*Zeemaneffekt*), while Hund (*l.c.* above) gives a list of papers on the multiplets in the Sc–Ni spectra. A useful review is given by Meggers:

MEGGERS. "The Periodic Structural Regularities in Spectra as related to the Periodic Law of the Chemical Elements," *Proc. Nat. Acad. Sci.* 11, 43 (1925)—

while the following paper gives a mass of useful data, admirably arranged, whose interest is wider than the title suggests:

RUSSELL. "A List of Ultimate and Penultimate Lines of Astrophysical Interest," *Astrophys. J.* 61, 223 (1925).

The following list of periodicals in which most of the recent experimental work on spectra has appeared, with the names of some of the leading investigators, may be useful:

Phil. Trans. and *Proc. Roy. Soc.* (Catalan, Fowler and his collaborators).
Phil. Mag. and *Phys. Rev.* (Millikan).
Astrophys. J. (Anderson, King, Russell, Saunders).
Proc. Nat. Acad. Sci., *J. Opt. Soc.*, *Science* (Kiess, Meggers, Walters).
Ann. der Phys., *Zeit. f. Phys.*, *Naturwiss.*, *Phys. Zeit.* (Back, Bechert, Catalan, Gieseler, Grotrian, Laporte, Paschen, Sommer, Sponer).

It may be of interest to mention that much of the work has been done under schemes of co-operation by different laboratories. These might well be extended.

CHAPTER XV

MAGNETISM AND CHEMISTRY

1. General Principles. Polar and Non-polar Compounds

DURING the last few years great progress has been made in the electronic interpretation of chemical valency. It is unnecessary here to consider in detail the chemical side of the problem, but a brief discussion will be given as to how far the magnetic properties of molecules and complex ions are in agreement with the chemical theories as to their electronic structure. While static atom models will be left on one side, this does not imply a scorn of the famous original Lewis-Langmuir " cube " (or " octet "), for, from the point of view of " economy of thought," the cube has been, and still is, of the utmost value. Many of the essential features of the Thomson-Kossel-Lewis-Langmuir theories are quite independent of particular atomic models; and Lewis, and chemists generally, now regard " cubes " merely as stepping-stones towards dynamic models of the Bohr type.

Although there may be no sharp line of demarcation, there are two types of combination between atoms which may be distinguished—polar and non-polar. Polar linkage is illustrated by NaCl, non-polar by Cl_2. In a sense, typical polar compounds may be said not to form chemical molecules (Campbell). In solution, sodium chloride exists as Cl^- and Na^+ ions, one electron having been transferred from the Na to the Cl. In Cl_2, on the other hand, the two atoms unite into a definite individual entity, the chlorine molecule; of this the simplest interpretation is to suppose that electrons may be " shared " by the two atoms, or, in terms of the dynamical theory, that electrons may move in orbits under the influence of two centres of force. The simplest type of orbit would be approximately elliptical, the electron moving round two positive charges at the foci of the ellipse.

One of the chief merits of the Lewis-Langmuir theories is that electro-valency (involving electron transfer) and co-valency (involving electron sharing), both appear as resulting from the tendency of the electrons to form stable configurations about the atomic nuclei; these stable configurations have numbers of electrons equal to those in the inert gas atoms (2, 10, 18, 36, 54 and 86) which, as standards of atomic stability, form the key to the problem of molecular structure. As already mentioned, there are also sub-standards with 28, 46, 68 and 78 electrons. Langmuir's first postulate may be most simply expressed, using terms previously discussed (Chs. V and XIV), by saying that the electrons tend to build up completed configurations about the nuclei. For polar compounds this at once covers a vast range of chemical facts. Non-polar compounds require further consideration. Langmuir's second postulate states that atoms may be coupled together by duplets (electron-pairs) held in common by the completed sheaths of the atom (the outer layers of electrons in the static model). Thus Cl requires one electron to form the argon configuration. Two Cl atoms may unite and attain the completed configuration round each nucleus if a pair of electrons (or electronic orbits) may be shared in common.

The insistence on "duplets" as invariably constituting the covalence link has given rise to many difficulties; Main-Smith, from a consideration of many compounds, concludes that there is no simple rule for determining the number of electrons in a chemical bond, and that every bond has to be investigated individually. One shared electron per bond is frequently indicated by the evidence from compounds with atoms of valency greater than four.

From a dynamical point of view, the existence of one or two shared orbits in binary molecules would seem quite feasible, without it being necessary to suppose that the arrangement of the orbits about the individual atomic nuclei is unduly distorted from that characteristic of the completed configurations of free inert gas atoms. The sharing of more than two orbits is more difficult to imagine. In the cube models, Cl_2 (or F_2) is represented by two cubes joined along an edge (two electrons shared), and O_2 by two cubes joined by a face (four electrons shared), but in N_2 it is necessary to imagine that the two atomic nuclei enter into a single cube. While a dynamical "translation" can readily be given of the Cl_2 and N_2 static structures, O_2 would present formidable difficulties. The dynamical structure of these molecules will be discussed in the next section in connection with their magnetic properties.

With the two postulates so far given the valency theory would "account for" unlimited compounds which do not exist. A restriction must be imposed. This is provided by a third postulate—that the residual charge on each atom or group of atoms tends to a minimum. A point which has been discussed in connection with the Bohr theory (Ch. XIV) must also be remembered—that the most stable configuration depends markedly on the central positive charge.

When atoms combine, the most firmly bound electrons in each will continue to move in orbits which differ little from those in the free atom, this being shown clearly by the fact that X-ray spectra are uninfluenced by combination unless transitions from outer orbits are involved. (Thus K and L absorption edges exhibit fine-structure peculiarities which do depend on the mode of combination of the atom.) The least firmly bound electrons, which may be crudely referred to as " outer electrons," since they are moving, during part of their orbits, at the outermost part of the atom, may be completely transferred to another atom. They may also be shared, moving in orbits whose forms differ widely from those in the free atom, being characteristic of motion about two or more centres of force. They are " molecular electronic orbits," whose mathematical treatment would present great difficulty. Possible orbits will be restricted by quantum conditions, which are as necessary to account for molecular as atomic stability. The orbital curves may be of the Cassinian oval class (Morgan) in diatomic molecules, including as a special type the figure-of-eight (Lowry), which may represent the limiting case of electron sharing preceding electron transfer. The fertility of this conception has been emphasized by Main-Smith, but as yet the theory is in the qualitative stage.

The elementary magnetic moments which have so far been discussed have in the main corresponded to individual atoms or simple ions. In substances such as the halides of the alkali or alkali-earth metals the ions in solution assume electronic configurations, by transfer of electrons, similar to those of the inert gases (Ch. XII, Table XXXV), and in agreement with theory the ions are diamagnetic ; ions with incomplete configurations, which occur in the transition elements, exhibit paramagnetic properties. These have been sufficiently discussed, and the general conclusions indicate the lines for attack on the problems raised by the susceptibilities of molecules and complex ions. These will now be considered.

2. Simple Molecules

It will be convenient to collect together (from Ch. XII) some of the results for gram-molecular susceptibilities to which reference will be made. The number of electrons in the molecule is also given :

$-\chi_M \times 10^6$.					
(Soné)		(Wills and Hector)		(Pascal)	
2 H_2	4·0	2 He	1·7	10 NH_3	19
14 N_2	7·4	10 Ne	6·1	34 Cl_2	41·5
22 CO_2	18·7	18 A	16·5		

TABLE XXXIX.—Gram-molecular Susceptibilities.

For hydrogen, with only two electrons, it is possible to calculate the areas of the orbits on the same lines as in section 2 of the last chapter. Assuming random orientation of two similar orbits, from XIV (3), the following results are obtained :

$$H_2 \quad \overline{r^2} = \cdot 7 \times 10^{-16} \qquad \sqrt{\overline{r^2}} = \cdot 83 \text{ A.U.}$$

On the ordinary theory the mean square projected radius would be $\frac{2}{3}$ times as great. Now Glaser's experiments (Ch. XII, sect. 4) indicate that when the pressure is small the molecular susceptibility is three times as great. From this an estimate of the maximum projected value of $\overline{r^2}$ may be obtained—

$$\overline{r^2}_{\text{max}} = 1 \cdot 4 \times 10^{-16} \qquad (\sqrt{\overline{r^2}})_{\text{max}} = 1 \cdot 2 \text{ A.U.}$$

From the band (or many-lined) spectrum, it may be calculated that the moment of inertia of the hydrogen molecule is of the order $1 \cdot 8 \times 10^{-41}$ gm. cm.^{2}, so that the distance between the two atomic nuclei is about $\cdot 5 \times 10^{-8}$ cm. This is considerably smaller than the radii of the electronic orbits as above calculated, so that the hydrogen molecule may be regarded as a system consisting of two electrons rotating about a central positive charge of two ; the orbits, however, are much larger than those in helium, although the central charge is the same. Thus, while the union of two hydrogen atoms into a stable molecule illustrates the tendency to formation of configurations, in which the number of electrons is equal to those in inert gas atoms, the quantum numbers characterizing the normal hydrogen molecule orbits must be greater than those for the helium atom. It would seem as though movement of the electrons in orbits of small quantum number, such as (1, 1) orbits, whose dimensions would be comparable with the internuclear distance, is incompatible with the stability of the molecule as a whole.

It may be that the observed diamagnetic susceptibility is too high—though the measurements of Soné and of Wills and Hector are in good agreement—for calculations on the lines indicated by equations (4–6) in Chapter XII lead to lower values for the radii than those deduced from the diamagnetism. Accepting Smyth's conclusion that 16·4 volts corresponds to $H_2 \longrightarrow H_2^+ +$ electron, the maximum value for the mean square radius (taking the "effective nuclear charge" as necessarily between 1 and 2) comes out as less than $\cdot 5 \times 10^{-16}$ cm.^{2}. (If Smyth's conclusion is correct the total quantum number *n* cannot be greater than 2.)

This lack of agreement indicates the nature of the problems raised even by simple molecules, and the significance of the magnetic properties in connection with them. Only a crude, tentative and provisional model of the hydrogen molecule can be suggested, with all due diffidence. The two nuclei rotate about their common centre. The axis of rotation of the nuclei may more conveniently be taken as defining the axis of the molecule than the line joining them, since, except at very low temperatures, rotation occurs. In a magnetic field there will be a tendency for the molecule to orientate with the plane of the nuclear rotation at right angles to the field. (The rotating nuclei form a system having a mechanical and magnetic moment, whose energy will depend on orientation, so that spatial quantization rules should apply.) It is when this orientation can establish itself—this will be favoured by low pressures, so that there are fewer collisions—that the enhanced diamagnetic susceptibility is found, as in Glaser's experiments. The electron orbits may therefore be supposed normally to be parallel to the plane of the nuclear rotation, and to be restricted to this plane. Quantum stability conditions would then be satisfied, and the factor 3 would be accounted for, as shown in Chapter XII, section 4. The electrons move in opposite directions in orbits for which the total quantum number is greater than one.

For molecules containing a considerable number of electrons calculations of mean square orbital radii from the diamagnetic susceptibility are of less value. It is, however, the contributions of the "outer electrons" which is most important, owing to the greater orbital areas, as in neon and argon (Ch. XII, sect. 3). In this connection it is interesting to note that the susceptibility of N_2 is only slightly greater than that of Ne. According to Langmuir, the two nitrogen atoms form a single "cube," which contains the two nuclei. The nuclei retain their two K electrons; associated with the nuclear pair are two more electrons, while the remaining eight form a configuration similar to the outer eight in neon. The magnetic data seem to support the dynamical equivalent of this suggested structure, in favour of which Langmuir adduces the low boiling-point of nitrogen, and the difficulty of dissociation. Chlorine has a susceptibility more than twice as great as argon—supporting the view that the two chlorine atoms unite into a structure dynamically equivalent to two argon "cubes." In NH_3, the three hydrogen electrons may be supposed to complete the eight round the nitrogen atom. The structure will be similar to that of neon, but owing to the lower nuclear charge (7 instead of 10) and possibly to the hydrogen positive nuclei being exterior to the configuration, the orbits will be larger, and hence the susceptibility greater.

For N_2 considerations similar to those for H_2 will apply as to the enhanced susceptibility at low pressures. For CO_2 the problem is more complicated, and not enough is known about the rotations of the nuclei to make any definite conclusions possible. The susceptibility is in agreement with a triple neon-like structure.

Whatever difficulties there may be in the way of giving a precise dynamical picture of the nitrogen molecule, it seems legitimate to conclude that the electrons form a molecular "closed configuration," analogous to the atomic closed configurations of the inert gas atoms. To the oxygen molecule Langmuir assigns a different structure—two cubes are supposed to be joined face to face. This raises difficulties in dynamical interpretation—for four electrons have to be shared—and also the widely different structures for oxygen and nitrogen do not seem compatible with the physical similarity of the two gases. In discussing the paramagnetism of oxygen, it was concluded that the molecule, with a moment corresponding to two Bohr magnetons, was analogous to an atom in a ^3S state—that is, that it had two electrons rotating in the same direction (and with the same azimuthal quantum number), in addition to those in a closed configuration. This would correspond to the two nuclei being within a single Langmuir cube, which would be much more in harmony with the physical and chemical properties of the molecule. As two electrons cannot move in orbits characterized by exactly the same quantum numbers (Pauli), it must further be supposed that the total quantum number for one of the orbits is greater than that for the other, so that one of the electrons will be more loosely bound. This may account for the formation of the ClO_2 molecule, in which one of the O_2 electrons, by transfer or sharing, completes the inert gas atom configuration round the Cl. There would then remain one unbalanced orbit, and in agreement with what might be anticipated, Taylor and Lewis have found that a solution of ClO_2 in carbon tetrachloride is paramagnetic. The gram-molecular susceptibility is $1,310 \times 10^{-6}$, indicating a Weiss magneton value of about 8·7. Paramagnetism would, indeed, be expected in general for "odd" molecules, such as ClO_2 and NO, with 15 electrons. Soné has found that NO_2 is also paramagnetic. The magnetic properties of NO are in harmony with the above view as to the structure of N_2 and O_2. In NO the two nuclei are within a single cube, there being one external electron (that is, one electron in addition to those in a closed configuration). Although a structure can be assigned to oxygen which will account for its paramagnetism, this still remains somewhat anomalous, for there is no obvious reason why the state in which the two electrons are unbalanced is the most stable, since there seems to be a general tendency for electron orbits to balance magnetically when this balance is not incompatible with the energy requirements.

While the magnetic properties of molecules can be reasonably well interpreted in terms of dynamic models of the type indicated by the general Bohr theory, as yet the pictures are vague. By analogy, however, the useful features of the older chemical static models are retained, and the dynamical model is much richer in possibilities. In some cases the magnetic data enable very definite conclusions to be drawn as to molecular structure; and the suggestions made may be sufficient to indicate the promise of further magnetic investigation in assisting in the elucidation of molecular-structure problems.

3. Complex Ions

The magnetic susceptibilities of a number of complex salts have been measured by Pascal and others, but the most systematic survey of a large series is provided by the work of Rosenbohm on the metal ammines (1919). Welo and Baudisch (1925) have collected previous results, and made new measurements on the complex cyanides and related compounds of iron. Most of the measurements have been made on solids, but usually, unfortunately, at only one temperature. In deducing the moment of a paramagnetic ion, corrections may be applied in the usual way for diamagnetic groups, though they are somewhat uncertain owing to the possibility of unknown constitutive effects. The Weiss magneton values (p) are often calculated on the assumption that a Curie law—$\chi T = C$—holds, and though this may be approximately true, there are frequently wide divergences (cf. Table XI, Ch. VI). (For details as to the calculations see Chapter VI, section 1, and cf. Chapter VII, section 2, on the rare-earth salts.) Any *p* values will therefore only be given to the nearest whole number, and must be regarded as approximate.

The results have been discussed by Welo and Baudisch, and by Jackson, and their treatment will be largely followed. This is based on Sidgwick's interpretation of the structure of co-ordination compounds in terms of the Bohr theory. He finds that complex ions reveal the tendency towards the formation, either by electron sharing or electron transfer, of stable symmetrical configurations of the inert-gas type, and that any group in the ion complex may be regarded as making a definite contribution to the electrons associated with the central atom. Sidgwick's views may be most clearly illustrated by some specific examples. Cobalt forms a large number of ammino-compounds, most of which may be referred to one of seven series. Adopting the Werner symbolism, these may be represented by the general formulæ in the following table:

I	$[Co\ A_6]\ R_3$
II	$[Co\ A_5\ R]\ R_2$
III	$[Co\ A_4\ R_2]\ R$
IV	$[Co\ A_3\ R_3]$
V	$[Co\ A_2\ R_4]\ M$
VI	$[Co\ A\ R_5]\ M_2$
VII	$[Co\ R_6]\ M_3$

$A = NH_3,\ H_2O$
$R = Cl,\ CN,\ NO_2$
$M = K,\ Na$

TABLE XL.—Cobaltammines.

The compounds ionize as indicated by the square brackets—$[Co\ A_6]\ R_3$ into $Co\ A_6^{+++}$ and $3R^-$, $[Co\ A_2\ R_4]\ M$ into $[Co\ A_2\ R_4]^-$ and M^+. There is a transfer of electrons between the groups inside and outside the bracket. The groups surrounding the central atom inside the bracket must be joined by non-polar links, and by considering the whole series, conclusions may be drawn as to the number of electrons shared or transferred by a given group. Outside the bracket, R must remove one electron, M add one. Inside the bracket A contributes two electrons to the central atom, one by transfer and one by sharing; while R contributes one by sharing. It will then be seen that there are associated with the Co atom (initially with 26 electrons), in all the above types of compounds, 36 electrons—the number in the next higher inert-gas atom Kr. It would be expected that the cobaltammines, in contradistinction to the simple cobalt salts, would not be paramagnetic. This is confirmed by Rosenbohm's work. It should be noted that outside the bracket

SO_4, SO_3, etc., are equivalent to Cl_2; and that inside the bracket a CO group must be supposed to contribute two electrons (by sharing), and an NO group three (one by transfer, two by sharing); a group such as $NH_2.CH_2.CH_2.NH_2$ (en) is equivalent to two NH_3 groups. For the number of electrons associated with the central atom the term " effective atomic number " is convenient. Denoting this by z, and the atomic number by Z,

$$z = Z + a + 2b + c \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where a is the number of links supplying one electron (as with Cl, CN, NO_2 inside the bracket), b those supplying two (as NH_3, H_2O), and c is the number of electrons added by transfer. As examples:

For $[Co(NH_3)_5Cl](NO_3)_2$ $\quad z = 27 + 1 + (5 \times 2) - 2 = 36$

For $[Fe(CN)_5NH_3]Na_2$ $\quad z = 26 + 5 + (1 \times 2) + 2 = 35$

The general results may now be considered, beginning with those for members of the first transition series of elements, for which the magnetic properties of the simple salts have been most investigated (see Table XX, Ch. VII, etc.). The following are some of the results given by Welo for iron compounds, χ being the mass susceptibility observed, and χ_{Fe} the net gram-atomic susceptibility of the iron. The Weiss magneton value p was taken as proportional to the square root of χ_{Fe}, the value 10·2 for $K_3[Fe(CN)_6]$ being deduced from Pascal's measurements on a dilute solution.

	Salt.	$\chi \times 10^6$.	$\chi_{Fe} \times 10^6$.	p.
Ferric	$K_3[Fe(CN)_6]$	9·0	3,080	10·2
	$Na_3[Fe(CN)_5NH_3] + H_2O$	9·5	2,650	9
	$Na_3[Fe(CN)_5NO_2]$	8·7	2,717	10
	$Na_2[Fe(CN)_5H_2O] + H_2O$	10·4	2,888	10
	$Na_2[Fe(CN)_5NO] + 2H_2O$	− 3·5	− 4	0
Ferrous	$K_4[Fe(CN)_6] + 3H_2O$	− 4·1	5	0
	$Na_3(Fe(CN)_5NH_3] + 6H_2O$	− 2·8	68	1
	$Na_4[Fe(CN)_5NO_2] + H_2O$	− 1·5	58	1
	$Na_5Fe(CN)_5SO_3 + 2H_2O$	− 3·3	10	1
	$Na_3[Fe(CN)_5H_2O] + H_2O$	+ 41·2	1,307	7
	$Fe(CO)_5$	− 3·8	− 54	0

TABLE XLI.—SUSCEPTIBILITIES OF COMPLEX IRON SALTS.

For the first four salts, the effective atomic number is 35; the results may be expressed by

$$\text{Fe } 35 \qquad p \fallingdotseq 10.$$

In the next salt NO contributes three electrons, so that $z = 36$, as also in the first three salts of the ferrous series. In iron carbonyl (liquid) the CO group contributes two electrons. Generally, therefore,

$$\text{Fe } 36 \qquad p \fallingdotseq 0.$$

The constitution of the fourth ferrous compound is uncertain. (It would seem probable that it has only four (CN) groups.) The fifth was difficult to prepare, and some specimens were found to be diamagnetic. It is therefore doubtful whether the paramagnetic susceptibility recorded is characteristic of the pure salt. A residual paramagnetism is generally indicated for the ferrous compounds. This may be real, but in view of the difficulty of ensuring purity of the salts, and the uncertainties in applying the diamagnetic corrections, no definite statement can be made.

Rosenbohm measured the susceptibilities of some sixty cobaltammines, of which all were diamagnetic except two of the triammines which were slightly paramagnetic. In all the compounds the effective atomic number of the Co is 36.

$$\text{Co } 36 \qquad p \fallingdotseq 0.$$

Rosenbohm found that the gram-molecular susceptibilities could be represented to within a few per cent. by a Pascal formula (XII, 3),

$$\chi_M = \Sigma a \chi_A + \lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Using the Pascal values for the diamagnetic groups (Tables VII and XXXII), he deduced the following values for λ for the cobalt in the different types of compounds:

Cobalt.	$\lambda \times 10^6$.
Hexammines	+ 55
Pentammines	+ 60
Tetrammines	+ 73
Triammines	+ 97

TABLE XLII.—THE CONSTITUTIVE CONSTANT FOR THE COBALTAMMINES.

The precise significance of the increase in λ is by no means clear, but a suggestion may be offered. In passing from the hexammines to the triammines the central Co atom loses, by transfer, 3, 2, 1, and 0 electrons respectively, so that its resultant positive charge decreases. It would be anticipated that the firmness of binding of the shared electrons from the co-ordinated groups would also decrease, so that the closed configuration of 36 electrons would become less stable in an applied field. Small relative changes in orientation of parts of the structure, possessing a resultant moment, might then become possible, and residual paramagnetic effects would make an appearance.

The ammines of chromium, nickel and copper were all paramagnetic. Some results for a few of the compounds, chosen at random, are given in the following table, in which the final column gives the mean rough p value deduced from all the compounds measured by Rosenbohm. The gram-molecular susceptibility is denoted by χ_M, and p may be calculated from the formula (cf. Ch. VII, sect. 2)

$$p = 7{\cdot}6\sqrt{\chi_M \times 10^3} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

z is the effective atomic number of the central atom in the complex ions.

Central Atom Z.	z.	Examples.		p.	Mean p.
		Salt.	$\chi_M \times 10^3$.		
Cr 24	33	$[Cr(NH_3)_6]I_3$	5·64	18	19
		$[Cr(NH_3)_5Cl]Cl_2$	6·27	19	
		$[Cr(NH_3)_4Br_2]Br$	5·02	17	
		$[Cr(NH_3)_3(SCN)_3]$	6·28	19	
		$[Cr(OH_2)_6]Cl_3$	6·28	19	
		$[Cr(SCN)_6]K_3$	5·63	18	
Ni 28	38	$[Ni(NH_3)_6]Br_2$	4·45	16	16
		$[Ni(OH_2)_4en](NO_3)_2$	4·46	16	
	34	$[Ni(NH_3)_4]SO_4$	2·94	13	13
Cu 29	35	$[Cu(NH_3)_4](NO_3)_2$	1·41	9	9

TABLE XLIII.—Susceptibilities of Complex Salts.

Although much more work is necessary before it will be possible to deduce p values with desirable precision, the mean values are quoted because they do seem to have significance. Thus, of the 29 chromium salts Rosenbohm investigated, 21 gave $p = 19$ to within a fraction of one per cent.

The following table gives a rough indication of the magnetic moments of ions of complex salts of elements of the first transition series, Z being the atomic number, and z the effective atomic number:

	Cr.	Ni.	Cu.	Fe.	Fe.	Co.		Ni.
Z	23	28	29	26	26	27		28
z	33	34	35		36		37	38
p	19	13	9	10	0	0		16

TABLE XLIV.—MOMENTS OF COMPLEX IONS OF ELEMENTS OF FIRST TRANSITION SERIES.

On comparing these p values with those of Table XX, it will be seen that familiar numbers reappear. Ions with a central atom of effective atomic number 36 have zero moment like the simple ions with 28 electrons. The ions with $z = 35$ have a moment approximately the same as ions with 19 (i.e. $18 + 1$) and 27 (i.e. $28 - 1$) electrons; while the complex Cr ion ($z = 36 - 3$) has the same moment as the Cr^{+++} ion with ($18 + 3$) electrons. Nickel is particularly interesting, as it is the complex ion with $z = 36 + 2$ which appears to correspond to the simple ion with $28 - 2$ electrons, the complex ion with $Z = 36 - 2$ having a definitely smaller moment. It is not difficult to devise distributions of electrons in the M and N levels which serve, in some measure, to correlate a number of these results; but until further data are available from which moments can be more precisely calculated, such speculations would be of little value. It is interesting to note that Rosenbohm found $[Zn(en)_3]Cl_2$ (with $z = 40$) to be diamagnetic. This may illustrate the tendency for diamagnetic configurations to be formed—a configuration of zero moment is always possible when there is an even number of electrons.

In $KMnO_4$ and $K_2Cr_2O_7$, Mn and Cr, as previously discussed, exhibit only a slight residual paramagnetism. It seems probable that there is a tendency towards the argon configuration which would be attained if each oxygen atom removed two electrons from, and each potassium atom added one electron to, the central atom.

The study of the magnetic properties of complex salts is as yet in its infancy. Independently of its purely magnetic interest, further more detailed research may shed some light on a number of physico-chemical problems—as to whether, for example, ions of simple salts, such as $NiCl_2$, in solution, are simple or complex. The ions in some cases are united by non-polar links with molecules of the solvent, but it is by no means clear how far such co-ordinated molecules may be differentiated from the "atmosphere" of solvent molecules which surround the charged ion. Some of the curves (e.g. Figs. 22–24) showing the variations in apparent ionic moment with concentration indicate that there is a wide range of phenomena which might well repay intensive chemico-magnetic investigation.

Rosenbohm's results for other complex salts may be briefly summarized. Rhodium ($Z = 45$) forms compounds of the type $[Rh(en)_3]Cl_3$, in which the effective atomic number is 54—the number of electrons in X, the next higher inert gas. These are found to be diamagnetic. The ruthenium ($Z = 44$) compounds are also diamagnetic, the effective atomic number being again 54, as in $[Ru(NH_3)_4Cl(NO)]Br_2$. The iridium ($Z = 77$) compounds are diamagnetic, and also those of platinum ($Z = 78$), whether they are of the tetrammine or hexammine type. For the iridium and platinic salts, such as $[Ir(NH_3)_5NO_2]Cl_2$ and $[Pt(NH_3)_4Cl_2]Cl_2$, $z = 86$—the niton number; but in the platinous salts, such as $[Pt(NH_3)_4]SO_4$ and $K_2[PtCl_4]$, $z = 84$. It appears again, as in the case of zinc, that when the number of electrons is even, there may be a configuration of zero moment, although the effective atomic number of the central atom of the complex ion differs from that of an inert gas. For the iridium compounds, the constitutive constant for Ir changed in a similar manner to that for cobalt (Table XLII) in passing from the pentammines to the triammines.

A number of isomeric compounds were investigated, and it was found that cis- and trans-modifications had the same susceptibility, as also mirror image isomers. Co-ordination isomers, on the other hand, such as $[Cr(NH_3)_6][Co(CN)_6]$ and $[Co(NH_3)_6][Cr(CN)_6]$, usually differed slightly.

Rosenbohm's work has the character of an admirable and comprehensive survey. Refined work is now necessary such as has been carried out for some of the simple salts as discussed in earlier chapters. All investigations on complex salts at the present time have a peculiar interest, for a clearer interpretation of the linkages between the constituent atoms and molecules would go far towards a solution of the baffling problem of the nature of the "forces" which are determinative of crystal structure.

4. Constitutive Effects

An account has already been given of Pascal's work (Ch. XII, sect. 1), and the main conclusions have been considered. In the course of his investigations Pascal measured the susceptibilities of hundreds of organic compounds—mainly liquids—and determined the constitutive constants corresponding to many types of linkage between different atoms. Some typical results will be briefly discussed, attention being confined to organic compounds.

Diamagnetic elements retain their natural magnetic properties practically unchanged when they form combinations of simple structure, so that it is possible to assign additive constants to them. The susceptibilities of compounds containing benzene rings and non-saturated groups usually differ from those calculated by adding the susceptibilities of the constituent atoms, but it is still possible to retain the additive constants unchanged by assigning a definite constitutive constant to each definite type of linkage, the general equation for the calculation being

$$\chi_M = \Sigma a \chi_A + \Sigma \lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

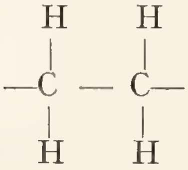
Some of the constitutive correcting constants deduced by Pascal as associated with various groups (per gram-molecule) are as follows:

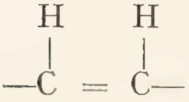
Group.	$\lambda \times 10^6$.
Benzene	$-1{\cdot}5$
Naphthalene	$-6{\cdot}3$
Indene	$-7{\cdot}7$
Ethylene	$+5{\cdot}7$
Diethylene	$+11{\cdot}0$
Acetylene	$+{\cdot}8$

(In this section the values given by Pascal are used. These are referred to water with $-\chi \times 10^6 = 7{\cdot}5$ as standard, so they are all probably about 4 per cent. too high.)

In the aliphatic non-saturated compounds, as the last three numbers show, the diamagnetism is diminished. Pascal states that this is not due so much to the smaller proportion of hydrogen as to the perturbing influence of the double (or triple) bonds, whose rôle is equivalent to that of paramagnetic elements. This suggested that an accumulation of multiple bonds might give rise to paramagnetism, but actually no magnetically pure organic substances were observed to be paramagnetic. (The behaviour of the cobaltammines may be contrasted.) The assignment of constants to "bonds," however, is liable to be misleading, as is shown by a consideration, for example, of the following series of groupings, for which the "gram-molecular" susceptibilities may be calculated from (4):

$-\chi_M \times 10^6$.

1. 
$-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-$ $\quad (2 \times 6\cdot2) + (4 \times 3\cdot0) + 0 = 24\cdot4$

2. 
$-\overset{\displaystyle H}{C}=\overset{\displaystyle H}{C}-$ $\quad (2 \times 6\cdot2) + (2 \times 3\cdot0) - 5\cdot7 = 12\cdot7$

3. $-C \equiv C-$ $\quad (2 \times 6\cdot2) - \cdot8 = 11\cdot6$

The diamagnetic susceptibility, on the theory which has been developed, depends essentially on the number and size of the electronic orbits—primarily the "outer" orbits (cf. sect. 2)—associated with the group. Now in the first group, each carbon nucleus may be regarded as forming the centre of an electronic configuration of a closed type—a Langmuir cube, or its dynamical equivalent. In the second and third, the "outer" electrons may be supposed to form a single closed configuration round the two nuclei together. The decrease in diamagnetism is at once accounted for, for the size of the electron orbits will be decreased owing to the increase in the effective positive charge controlling their dimensions. The small change in passing from group 2 to 3 is noteworthy. It suggests that the hydrogen nuclei in the ethylenic group are inside the electronic configuration.

Analogous changes to those in the groups containing two carbon atoms are observed in groups with a carbon and a nitrogen atom. When united by a single bond (as in amines), the simple addivity law holds; for double bonds (as in oximes, hydrazines), triple (nitriles), and quadruple (carbylamines), Pascal finds for $10^6\lambda$ the values 8·5, ·8 and ·4 respectively. The significance of the numbers becomes clear, on the above views, on consideration of the calculated susceptibilities for the following groups:

		$-\chi_M \times 10^6$.
1.	$-CH_2-NH_2$	24
2.	$-CH=NH$	9·5
3.	$-C\equiv N$	11·2
4.	$-N \equiv C$	11·6

Multiple bonds may be regarded as marking regions on the symbolic map of the molecule where there is a concentration of positive charges. The electrons associated with these will move in smaller orbits, so that the normal diamagnetic effect of the atoms is reduced.

As, in general, the presence of double bonds decreases the diamagnetism, the fact that a benzene ring formation results in an increase in the diamagnetism is noteworthy. It suggests that there is no concentration of positive nuclei, the six carbon atoms in the ring being spaced at equal intervals. There may be a slight increase in the size of the orbits associated with any one of the carbon atoms owing to the influence of other parts of the molecule. For mononuclear carbon atoms (that is, atoms associated with a single ring) Pascal calculates that $\lambda \times 10^6 = -\cdot 25$ (giving $6 \times -\cdot 25 = -1\cdot 5$ for the benzene grouping); and for binuclear carbon atoms $\lambda \times 10^6 = -3\cdot 2$, suggesting that the orbits round such carbon atoms are increased still more in size owing to the influence of the remaining portions of two rings.

That oxygen should usually have a diamagnetic effect appeared at first surprising. It is, however, the molecule which is paramagnetic; molecular susceptibilities depend on the electronic configurations associated with groups of atoms, and all that is involved is that oxygen atoms usually unite into diamagnetic groups with other atoms. When the oxygen atom is united to two different atoms, as in alcohols, its susceptibility constant is given by

$$\chi_{0'} = -4\cdot 8 \times 10^{-6}$$

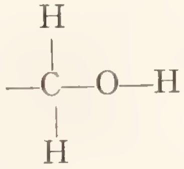
but when united by a double bond to a single carbon atom, as in aldehydes and ketones,

$$\chi_{0''} = +1\cdot 8 \times 10^{-6}$$

A consideration of groups suggests that the paramagnetism is only apparent.

$-\chi_M \times 10^6.$

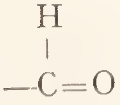
1.



$$-\overset{H}{\underset{H}{C}}-O-H$$

20

2.



$$-\overset{H}{C}=O$$

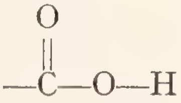
7·4

In the second group the C and O nuclei may again be supposed to form a single centre about which the outer electrons associated with them revolve.

When there are two oxygen atoms, one singly and one doubly bound, as in the acids and their anhydrides, the sum of their susceptibility constants is not $\chi_{O'} + \chi_{O''}$ as above given.

$$\chi_{O_2} = \chi_{O'}' + \chi_{O''}' = -8{\cdot}3 \times 10^{-6}$$

A comparison of a group susceptibility with that of the alcohol group above, however, suggests again that there is no fundamental anomaly.

	$-\chi_M \times 10^6$.
 $-\overset{\displaystyle O}{\overset{\|}{C}}-O-H$	17·5

Interpreted in the light of the usual theory, with the number and size of the electronic orbits determining the diamagnetic susceptibility, Pascal's results seem, on the whole, to fit in remarkably well with the dynamical conception of molecular structure. The "shapes" of the molecules, chain-like or ring-like, may be regarded as defined by lines joining the atomic nuclei. Round the nuclei the most firmly bound electrons—in the lighter elements, only the K electrons—will revolve in orbits which are practically the same as those in the free atom. The nuclei are linked together by shared-electron orbits. The outer electrons associated with the atoms will revolve in orbits which will be orientated in some definite way with respect to the lines joining nuclei in their neighbourhood. The nuclei are the centres about which definite electronic configurations will be formed. The size of the orbits is influenced mainly by the positive charge on the nucleus with which they are most directly associated, but also, to a greater or less extent, by the charges on neighbouring parts of the molecule. At regions indicated by multiple bonds, two or sometimes more nuclei may be drawn more closely together so as to form single centres for outer electrons, whose orbits will be reduced in size. The general conception can only be presented vaguely, but even in vague outline it seems of immense assistance in enabling observed phenomena to be interpreted; and in itself it is not unduly complicated.

The image of a complex molecule, if it is to bear any relation to reality, must be complex. Even atoms are complicated structures, and in molecules the upbuilding process, with nuclei and electrons as the materials, is carried on to a further stage.

It has only been possible here to give a very inadequate survey of Pascal's magneto-chemical researches, mainly by means of illustrative examples. His work extended over an enormous range of organic compounds of the most diverse type, and a re-examination of his data, on the basis of modern electronic theories of valency and molecular structure, may be commended to chemists. It seems that a more detailed consideration of some of the results could not fail to shed a flood of light on many disputed problems of chemical theory.

5. Alloys. Crystals

Alloys have been mainly investigated with respect to their ferromagnetic properties, and a detailed consideration of the results is outside the scope of this book. An enormous amount of research has been carried out. It has been admirably reviewed by Auwers (1920), and reference must be made to his survey for fuller details. Here only a brief account will be given of some of the more general results, and of the conclusions which may be drawn from them.

It has been emphasized that ferromagnetism is only a particular case of paramagnetism, depending for its appearance on the paramagnetic atoms or ions being united into a definite kind of structure. In Weiss's equation for paramagnetics, $\chi = \frac{C}{T - \theta}$, θ may be positive or negative, typical ferromagnetics being distinguished by the fact that, for them, θ is large and positive. In a sense, the distinction is arbitrary. If experiments on the magnetic properties of alloys of ferromagnetic metals are carried out at room temperature, absence of ferromagnetism may be due simply to the Curie-point being lower than this. This must be borne in mind in considering alloys, for generally they have been examined for ferromagnetism only, and investigations of their para- (or dia-) magnetic susceptibilities over a range of temperatures have not been carried out. The effect of different elements in changing the Curie-point is well illustrated by a series of ferromagnetic manganese compounds:

Compound.	Curie-point. ° C.
MnP	18–25
MnAs	40–45
MnSb	320–330
MnBi	360–380

It is found generally that definite chemical compounds of ferromagnetic with other metals are non- (ferro-) magnetic. As typical of a large number of binary compounds may be instanced FeSi, $FeAl_3$, $FeSb_2$, $FeZn_7$; compounds of Co and Ni with Si, Al, Sb, Zn; also Co_2Sn, CoSn, NiBi, $NiMg_2$. Fe_3Sb_2 and Ni_2Mg seem to be exceptions to the general rule. Compounds with "metalloids" are ferromagnetic, as Fe_5B_2.

Mixed crystals, with the ferromagnetic metal as solvent, retain their ferromagnetism; with the non-magnetic metal as solvent, they are generally non-magnetic. The effect of an ideal process of gradually adding increasing amounts of a non-magnetic metal to a ferromagnetic crystal may be considered. The "magnetizability" will decrease, becoming effectively zero when the proportion of non-magnetic metal is just sufficient to enable the compound which is richest in the ferromagnetic element to be formed; with further addition of the non-magnetic metal, the mixed crystal will remain non-magnetic. The curves for two ferromagnetic metals (Fig. 29) may be compared, but it should be noted that those refer (by extrapolation) to absolute zero. The desirability of extending the measurements on alloys generally to much lower temperatures is obvious. For some mixed crystals such as Cu-Ni, Cu-Co, Cr-Ni, there is, for certain proportions of the metals, an apparent absence of ferromagnetism owing to the Curie-point being below room temperature.

While ferromagnetics generally form non-ferromagnetic compounds, manganese, which as a solid element is paramagnetic, shows a strong tendency to form compounds which are ferromagnetic. Of the binary compounds, besides those with P, Sb, As and Bi, whose Curie temperatures have been referred to, may be mentioned Mn_3Al, $MnAg_2$, and Mn_4Sn. Ferromagnetism is most marked in the ternary alloys named after their discoverer, Heusler (1898). An alloy of the following composition—

Al	15	per cent.
Mn	23·5	,,
Cu	61·5	,,

has magnetic properties closely resembling those of nickel. The composition of the most strongly magnetizable alloy is approximately

Al	10	per cent.
Mn	20	,,
Cu	70	,,

The Al in these manganese bronzes can be replaced by Sn, As, Sb, Bi or B without loss of the ferromagnetic properties. Heusler has concluded (1912) that the essential "carrier" of the ferromagnetism is a compound which may be symbolized

$$[Al(Mn,Cu)_3]_x$$

one atom of Al being associated with three of Mn and Cu together (the Mn and Cu forming an isomorphous mixture). Similar relations seem to hold for the tin manganese bronzes (Heusler and Semm, 1914).

Although the maximum intensity of magnetization (in the usual sense) of ferromagnetic metals and alloys at a given temperature is approximately the same for different specimens, the form of the hysteresis curves depends very markedly on the thermal treatment. This influences the microcrystalline structure. The dependence of the properties on the crystal size was investigated by Thompson, who obtained the following results for two specimens of "pure" iron which had undergone different thermal treatment :

	Number of Crystals per cm.	B for H = 95 gauss.	Coercive Field. H_c gauss.
1	270	18,500	2·0
2	690	18,400	5·0

This suggests that modifications in the hysteretic properties brought about by comparatively small amounts of other elements may in some cases be due to their influence on the size of the crystals. (In Al, Si and P steels, however, the influence of the added elements is probably mainly of chemical origin, arising from their power of combining with oxygen.) The coercive field for an iron-mercury alloy is very high (of the order 370), of tungsten-steel (3–8 per cent. tungsten) about 60, and of "stalloy" —an iron alloy containing silicon—low. Most remarkable is the recently discovered "permalloy"; this special name has been given to iron-nickel alloys with about 80 per cent. Ni and 20 per cent. Fe. (Analysis of a good specimen gave 78·23 per cent. Fe, 21·35 per cent. Ni, traces of Co, Mn and other elements.) The saturation intensity of ferro-nickels at room temperatures varies almost linearly with the composition, and that of permalloy is of the anticipated order. With suitable treatment, however, the "initial" permeability (under fields of ·001–·002 gauss) is very high ($\mu \doteqdot 10,000$), and saturation is practically attained in fields of a fraction of a gauss (so, for example, in the earth's field). The hysteresis loss per cycle is only about $\frac{1}{100}$ of that of the best silicon steels, corresponding to the almost negligible coercive field. In chemical and physical properties other than those associated with ferromagnetic hysteresis, permalloy shows no peculiarities. The crystalline structure is that of nickel, as in Fe-Ni alloys generally with more than 35 per cent. Ni. It seems probable that the key to the remarkable behaviour is to be sought in the size of the microcrystals, and their relation to each other, but as yet no evidence is available on this point.

The application of X-rays to the investigation of the crystal structure of ferromagnetics has led to the conclusion that there is no direct connection between crystal structure and magnetic properties (Wyckoff). This conclusion, however, seems rather too general. It has already been pointed out that no change in crystal structure would be anticipated at the Curie-point ; moreover, there should be no difference in the X-ray spectrograms of magnetized and unmagnetized substances, for the changes in lattice dimensions, as the magnetostrictive effects show, would be inappreciable. Above the Curie-point the changes in the magnetic modification of iron from β to γ and γ to δ are definitely associated with changes in crystal structure (see Ch. VII, sect. 2).

When diamagnetic atoms unite into crystals, the crystals are generally diamagnetic also, though there are exceptions. Thus, although the Ca atom in its normal ^1S state would be diamagnetic, the crystal is paramagnetic. The residual paramagnetism may be associated with the fact that the Ca atom can also assume the paramagnetic ^3S state. Definitely paramagnetic atoms, on the other hand, frequently form diamagnetic crystals —as Cu, Ag and Au. In these atoms it is the outer electronic orbits which give the atom a magnetic moment, and in a crystal these orbits can apparently balance in pairs—though residual effects are observed in Na and K. When the atomic paramagnetism is due to lack of balance among underlying orbits, as in the transition elements, the crystals are usually strongly paramagnetic, or even ferromagnetic. As chromium has a crystal structure similar to that of iron, it has seemed remarkable that it does not show ferromagnetism. The question is certainly obscure, but following the lines which have been indicated, it may be suggested that the development of ferromagnetism depends on there being some definite reciprocal relation between the " magnetic symmetry " of the paramagnetic carrier (the ion or atom) in the crystal, and the symmetry of the crystal as a whole. The crystal symmetry in metallic crystals seems to be primarily dependent on the number of loosely bound valency electrons which can couple together the constituent atoms, as is shown by the fact that elements in the same family generally form crystals of the same type.

In considering the magnetic properties of crystals, or of solids generally, it is important to distinguish between the actual " magnetic carriers " and the groups of atoms with which these carriers are associated. In ferric sulphate, for example —$Fe_2(SO_4)_3$—the carriers are the Fe^{+++} ions, with a magnetic moment of five Bohr magnetons. Two such carriers are associated with each $Fe_2(SO_4)_3$ group, the carriers being free to reorientate independently. The moment of an ion depends only on its electronic configuration, but this is attained as a result of the transfer (or in some cases sharing) of electrons between the atoms constituting the whole group. In metal crystals, similarly, there will be mono-nuclear carriers, and one or more of these may be associated with a group of atoms. In alloys there is sometimes evidence of definite groups, such as Fe_2Co and Fe_3Ni_2 (see Fig. 29). Associated with each group there may be a number of carriers with different moments; to the group as a whole a moment may be assigned, but this will not necessarily be characteristic of a particular carrier (cf. Ch. VII, sect. 2). There are probably such groups in crystals of elements, in particular of ferromagnetic metals. There is no definite evidence that the electronic configuration of each atom is exactly the same. Thus the " magnetic molecule " in nickel may be Ni_3 or Ni_5, and such a " molecule " may contain a number of carriers with different moments. This is suggested by the fact that in the alloys there are groups with three and five atoms. The moments deduced from the saturation intensities at low temperatures are mean values for each atom. Further low-temperature magnetic work on alloys, coupled with physico-chemical and crystallographic investigations, is highly desirable to elucidate these questions. It seems that many apparent anomalies may disappear with the realization of the group-carrier distinction. For the appearance of paramagnetism (of the ordinary, non-residual type) there must be ions or atoms with a magnetic moment free to reorientate. These carriers may acquire their characteristic moments as a result of electron transfers within a group. The groups unite into a crystal edifice. Ferromagnetism depends on the relation of the carriers to the groups, and the arrangement of the groups in the structure as a whole. The ferromagnetic properties of Heusler alloys is probably due to groups being formed in which there are paramagnetic carriers, and to the groups uniting into a crystal edifice in which, as a whole, similar relations hold as in typical ferromagnetics. There are, however, many difficulties and problems which will only be solved by further experimental and theoretical research.

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CHAPTER XVI

PROBLEMS. SUMMARY AND CONCLUSION

1. Atomic Stability

IN a book in which almost all the chapters have been concerned with problematical issues, " Problems " is hardly a distinctive heading. The miscellaneous problems to be considered are connected with the dynamics of atoms, and the structure of radiation ; while not primarily magnetic, they are of interest and importance in connection with general magnetic theory.

The properties of electrons—and of protons—can to a certain extent be interpreted in terms of classical electrodynamical theory. If, however, electrons had all the properties which the theory would attribute to electrical charges—in particular, if they radiated when accelerated—it has long been recognized that stable atoms would not be formed. The fact that electricity is " atomic," and that the " atoms " all have the same charge, physics is unable to " explain." It must be accepted, provisionally at least, as fundamental. The treatment of electrons as continuous surface or volume distributions of charge, except formally, is unjustifiable, for the continuous distributions, whose observed properties the theory can account for, are continuous in an entirely different macroscopic sense. That ordinary atoms are stable systems also cannot be explained. It may, however, be traced back to the existence of certain quantum conditions, and the attempt may be made to show that if these conditions are satisfied, then stable systems will be formed. The quantum theory postulates that " action " is atomic ; but the atomicity of " action " does not seem to possess the same fundamental character as the atomicity of electric charge. It has been suspected that there is some close relation between the constants h and e ; but so far, no significant physical connection between them has been found. When energy is quantized, the size of the quanta depend essentially on a frequency. This seems to introduce an arbitrary distinction between periodic and non-periodic systems, which suggests that the formulation of the quantum theory, in its present form, is unsatisfactory and partial.

The classical theory is inadequate. It is both too narrow and too wide. A quantum theory of some kind is necessary, but at present the quantum and classical theories cannot be fitted together into a single harmonious whole. Both require modification. Ultimately a single theory may be evolved which will embrace them both.

Provisionally, it must be supposed that atoms owe their stability to the fact that electrons in them move in orbits which satisfy quantum conditions for stationary states. The consideration of the stationary states which are found to exist enables deductions to be made as to the nature of these conditions. While all atoms are stable in a limited sense, in degree of stability there are wide differences, if the probability of existence of free individual atoms is taken as a criterion. The inert-gas atoms, in particular, are marked out as possessing electronic configurations towards which other atoms tend. They form a key to the problem of chemical combination, and it is natural to inquire in what way they are differentiated from other atoms—as to why they should form a key of this kind, in common with atoms generally possessing " closed configurations."

In the process of upbuilding of atoms imagined by Bohr, electrons are supposed to be added successively to an initially bare nucleus. Each electron enters into a possible orbit in which it is most firmly bound. When a new electron is added, the quantum numbers n and k characterizing the electrons already in the atom remain unchanged. It has been shown by Pauli that it is possible to extend this principle of the " permanence of quantum numbers " to the quantum numbers j and m which are required in the treatment of multiplet structure and the Zeeman effect. To each electron, quantum numbers n, k, j and m can be assigned such as are characteristic of the single series electron in alkali-metal-like atoms; when there are a number of electrons external to a completed configuration, the resultant quantum numbers (in particular the resultant m) have the nature of a vector sum of those of the individual electrons. (In the Heisenberg scheme, referred to in Chapter XIV, section I, k is treated as a resultant, with far-reaching consequences.) Pauli concludes, from a consideration of the electronic structure of atoms, that a general rule may be stated to the effect that in an atomic system there cannot be more than one electron in each uniquely defined quantum state. This rule leads to the modified Bohr electron distribution scheme, discussed in Chapter V. An n, k group is completed when there is one electron corresponding to each possible j, m state. (The number of possible states is deduced from those for doublet atoms—see Table XXVII.

For $k = 1, 2, 3 \ldots$ there are 2, 6, 10 . . . different quantum states.)

In the first two sequences in the periodic table, in the process of upbuilding, successive electrons enter orbits for which n has the smallest value, these corresponding to minimum energy, and the greatest firmness of binding. A minimum value of n does not, however, always correspond to the firmest binding, and underlying groups may then be left incomplete. When electrons enter a k subgroup, that group is generally developed until it contains its full complement of electrons, when the stable closed configuration is attained. In the inert-gas atoms all the k subgroups which have any electrons have the complete number.

The essential magnetic characteristic of closed groups is that their resultant magnetic moment is zero. The Pauli rules enable the number of electrons required to build up closed configurations to be deduced, but do not account for their peculiar stability. This would appear to be due to the absence of magnetic moment. On the one hand, there is a tendency for the number of electrons round a nucleus to be equal to the positive charge on the nucleus, so that there is no external electrostatic field (at a distance); on the other, there is a tendency for the magnetic moments of the electron orbits to compensate each other, so that there is no external magnetic field. While the tendency to "electric neutrality" is usually the stronger, the tendency to " magnetic neutrality " manifests itself in the formation of ions of the inert-gas-atom type. The two tendencies may assist or oppose each other ; both are subject to the quantum restrictions as to possible orbits in which the electrons may move.

The electrostatic tendency (both in respect to neutrality, and to the binding of electrons) may be expressed by the statement that the electrostatic energy tends to a minimum. An attempt to express the magnetic tendency in an analogous manner seems to lead to difficulties, for two similar electronic orbits balance when their moments are opposed, and the mutual potential energy is then a maximum. A statement in terms of resultant external field seems simpler—for the resultant field, whether electrostatic or magnetic, is a measure of the intrinsic energy of the system when this is considered as a whole.

The problem of the stability of molecules is probably to be approached in the same way as that of the stability of atoms. As discussed in the last chapter, " outer " and " shared " electrons in molecules may be regarded as moving under the influence of two or more centres of force, and their possible orbits must be restricted by quantum conditions. The tendency towards the formation of diamagnetic configurations is strongly shown, and many chemical facts may be correlated by supposing that molecules tend to be formed with electronic configurations resembling aggregates of inert-gas atoms. It may be noted, however, that molecules which have properties closely resembling those of inert-gas atoms with closed configurations do not necessarily have the same number, even of outer electrons. Nitrogen is a striking example. Assuming that there are two K electrons round each nucleus in the molecule, there remain ten electrons. Eight of these (two in orbits with $k = 1$, six with $k = 2$) can form a configuration similar to that of the outer electrons in neon. The question arises as to the nature of the orbits in which the other two electrons move. The properties of nitrogen are in favour of the view that two electrons are more firmly bound than the eight, suggesting that they are in orbits of smaller total quantum number. It seems hardly possible, however, that they should be moving in (1, 1) orbits under the influence of a resultant binuclear charge of 10. It is a big step from atomic to molecular quantum dynamics, even in the simplest cases!

Closely connected with the question of stability and electronic configuration is that of the symmetry of atoms, but very little can be said about it. There is a considerable amount of evidence as to the symmetry of molecules, but many of the deductions which have been made as to atomic symmetry are hardly justifiable. On consideration, the statement that carbon displays tetrahedral symmetry seems to imply nothing more than that in a molecule such as CH_4 (to take the simplest example) the four hydrogen nuclei are distributed tetrahedrally about the carbon nucleus. Similarly, in co-ordination compounds, the types of symmetry depend on the number of groups associated with the central atom. No definite conclusions can be drawn as to the symmetry of the free atom, and so as to the arrangement in space of its electronic orbits. It may eventually prove possible to make deductions as to the symmetry properties of ions in crystals; the foundations on which attempts might be based have been laid by Shearer, who has traced relations between the symmetry of molecules and crystals. It is, however, from the Zeeman-effect separations, which must depend essentially on orbital orientation, that most information is to be obtained as to the spatial arrangement of electronic orbits in atoms; but until a satisfactory physical interpretation of the significance of the Landé splitting factor, g, has been found, little progress can be made.

2. Weak Quantization and Orientation

The degree to which quantum restrictions enable stationary states to be precisely defined under various limiting conditions has been considered by Bohr, Ehrenfest and Tolman, and others. Slater has given an admirable discussion of the question, and his treatment will be largely followed. The nature of the problem is perhaps seen most clearly in considering the orientation of orbits in a magnetic field. The theory of spatial quantization has been discussed in Chapter V, and it has been shown that experiments confirm the general conclusions in a remarkable manner. If it is stated that the resolved angular momentum of an electron in the direction of an external field is to be quantized, difficulties are encountered when the external field becomes zero, for, physically, there can be no sharp distinction between the conditions when the field actually vanishes, and when it is indefinitely small. Adopting the Bohr treatment, however, the possibility of spatial quantization is regarded as arising from the fact that a new frequency—the Larmor precessional frequency—is called into play by the field; a quantum number may be introduced corresponding to this frequency. If the period of the Larmor precession is small compared with the time during which the motion of the system considered continues without interruption, then the quantization may be regarded as "strong"; the system will take up a definite orientation, and will assume the appropriate energy value corresponding to a definite possible stationary state. If the Larmor period is long compared with the "interruption period," then quantization (which can only be regarded as definite when the system passes through a complete cycle) will be weak—the system will be unable to enter a stable stationary state before interruption of its motion occurs.

For the Larmor frequency ν' and period τ'

$$\nu' = \frac{eH}{4\pi mc} \doteqdot 1{\cdot}4 \times 10^6 H \qquad \tau' = \frac{1}{\nu'} \doteqdot \frac{{\cdot}7 \times 10^{-6}}{H} \tag{1}$$

The Gerlach and Stern experiments may be considered as providing an illustration of the conception of strong quantization. With a field of the order of 15,000 gauss, for the Larmor period, $\tau' \doteqdot 5 \times 10^{-11}$ sec. With atoms of velocity 5×10^4 cm. per sec. the field region will be traversed in about 10^{-4} sec. (cf. Ch. IX). This time is long compared with the Larmor period, and the atoms will be fully orientated after passing through an insignificant portion of the field region.

Ordinarily, in a gas, it might be anticipated that spatial quantization would only occur to an appreciable extent if the time between collisions were long compared with the Larmor period. Slater points out that in the Glaser experiments on diamagnetic orientation (Ch. XII, sect. 4) the range of pressures in which the changes in susceptibility occur corresponds to times between collisions of the right order. It seems doubtful, however, whether there is any connection. Considering some typical results of Glaser (Fig. 52) with a field of about 4,500 gauss

$$\tau' \doteqdot 1{\cdot}5 \times 10^{-10} \text{ sec.}$$

The times T between collisions can be calculated from kinetic-theory data given by Jeans. For the gases investigated, the following approximate values for T_0 (at 0° C., 760 mm.) are obtained.

H_2 $\cdot 7 \times 10^{-10}$ N_2 $1{\cdot}3 \times 10^{-10}$ CO_2 $1{\cdot}1 \times 10^{-10}$

Changes in susceptibility occurred at about 600 mm. for H_2, 400 mm. for N_2 and 300 mm. for CO_2. Since T is inversely proportional to the pressure, it is certainly of the same order as τ'; but since T_0 is smallest for H_2, it would be expected, if there is a connection of the type considered, that the change in susceptibility (corresponding to orientation) would occur at a lower pressure for H_2 than for N_2 and CO_2, while what is observed is the exact opposite of this. It must therefore be concluded that the pressure at which orientation begins to manifest itself does not, in these particular experiments, correspond simply to the pressure at which the time between collisions becomes comparable with the Larmor electronic precession period. It has been suggested (Ch. XII and Ch. XV, sect. 2) that the orientation is connected with precession of the axis of the nuclear rotations. The Larmor precession period would be about 2,000 times as small as that given by (1) (depending on the resultant charge divided by the mass), and approximately twice as great for hydrogen as for nitrogen; but if it is this period which is determinative, and orientation is completely destroyed by collisions, it would be necessary to suppose that orientation can establish itself in a time much shorter than a single Larmor period, which appears very improbable.

In ordinary experiments in which paramagnetic susceptibilities are determined a similar problem arises. The quantum-theory interpretation of the magnetic moments is certainly sufficiently confirmed to show that the paramagnetic carriers are practically fully orientated (though not necessarily always with the same orientation) for almost the whole time. The precessional motion involved is definitely electronic, and the period will be given by (1). Now for oxygen the time between collisions (at 0°, 760 mm.) is approximately $1{\cdot}4 \times 10^{-10}$ sec. With the fields employed by Bauer and Piccard, and Wills and Hector (about 20,000 gauss), $\tau' \doteqdot {\cdot}4 \times 10^{-10}$. This is less than T_0 so that orientation would be able to occur between collisions. In the Wills and Hector experiments, however, pressures up to about 15 atmospheres were used. T then becomes considerably less than τ'. In the early Curie experiments, high pressures and relatively small fields were employed. There is, however, no indication of any marked change in the susceptibility with increasing pressure and decreasing field over the ranges which have been investigated. (If there was a tendency towards random orientation, it would be anticipated that the Weiss magneton value would tend to change from 14·2 to 10.) Similar considerations apply also to ionic susceptibilities, though the "mean life"—as the time between collisions—cannot be so readily defined. It is certainly desirable that experiments should be carried out on gases with as high pressures and as low fields as possible. (These would be complementary to the Glaser low-pressure investigations.) From the evidence available it must be concluded either that orientation occurs almost completely in a time that is small compared with the Larmor period, or that a collision can generally only produce a change of a quantum transition type—from one definite orientation to another. This seems quite possible; but it must be remembered that the Glaser experiments show definitely that frequent collisions do lead to a random orientation distribution. The conditions, however, are somewhat different from those when paramagnetic carriers are concerned.

Experiments of the Wood and Ellett type (Ch. XI) remain to be considered. Under the conditions which are required in the study of the Zeeman effect, the fields are large, and the atoms are usually far apart; the sharpness of the lines which can be obtained then shows that orientation is complete, or that the quantization is strong. In the experiments on the polarized resonance radiation from sodium and mercury vapours, the pressures are also very small (of the order 10^{-3}–10^{-4} mm.), and the time between collisions will be large (of the order 10^{-4} secs.), compared with the Larmor precession period even when the field is small. The interruption period will depend on the mean life of the atom in an excited state. It is in this connection that the differences in the behaviour of mercury and sodium assume significance. With mercury, the initial polarization was practically destroyed by fields of one gauss in the beam direction. Hanle's experiments show that on observation in the beam direction the effect of an increasing field is to produce a rotation of the plane of polarization accompanied by a gradual decrease in degree of polarization. A classico-quantum treatment strongly suggests that the extent of rotation will depend on the ratio of the mean life of the atom in the excited state (for mercury, the p_1 state) to the period of the Larmor precession; on this basis, Hanle estimates the mean life at about 10^{-7} sec., which agrees with the value calculated from the field required to produce depolarization, and by other methods. In order that a field may exert an appreciable influence on the polarization phenomena in experiments of this kind, it would appear, in general, that the Larmor precession period τ' must be comparable with the mean life T of the atom in its excited state.

$$\tau' \leqq a\mathrm{T} \qquad \mathrm{H} \geqq \frac{4\pi mc}{e\mathrm{T}} \cdot \frac{1}{a} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\mathrm{H} \geqq \frac{\cdot 7 \times 10^{-6}}{a\mathrm{T}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.1)$$

where a will depend on the magnitude of the effect, tending to a lower limit of the order unity if the field is to produce its maximum influence. Since the fields required to produce comparable effects on sodium and mercury are approximately in the ratio of 100 to 1, this suggests that the mean life of the excited sodium atom (in the p_1 or p_2 state) is some hundred times shorter than that of mercury.

Somewhat similar arguments apply to the case of an alternating field, as used in Breit and Ellett's experiment (Ch. XI). A field of 1·2 gauss is sufficient to produce practically the full quantizing effect on mercury. If the field is alternating, it would be anticipated that the normal effect would still be exerted if the period of the alternations remained longer than the mean life of the atom; if less than this, the quantizing would become indefinite. With a frequency greater than 10^7, Breit and Ellett found the influence to be negligible—indicating again a mean life of the excited mercury atom of the order 10^{-7} sec.

On the whole, the experiments on the influence of a magnetic field on the polarization of resonance radiation do seem to show fairly definitely that the time required for the establishment of strong quantization is of the same order as the Larmor precession period, though much further work is still required. If this view is correct, there certainly is a difficulty in connection with the influence of collisions on paramagnetic susceptibility measurements. It is possible that only a small fraction of the collisions are effective in disturbing the atoms or molecules from a definitely quantized state without removing them completely to another quantized state ; and this may be true also in Glaser's experiments. The mere statement of the difficulties, however, may be a step towards their solution.

In this section problems such as those connected with the fact that mercury resonance radiation may be almost completely polarized when there is no magnetic field have not been considered ; nor those connected with the mechanism by which orientation or reorientation is brought about. Orientation has already been discussed at some length (Ch. IX, sect. 4, etc.), and it has been shown that purely classical mechanical forces seem wholly inadequate to explain it. Slater introduces the conception of quantum forces which tend to bring a system into a possible stable stationary state ; these do not oppose the classical forces when an atom is actually in a stationary state, but in other cases may be capable of exerting a powerful action, which cannot be described in ordinary dynamical terms. This is a convenient formal way of stating a fundamental difficulty which remains to be solved.

3. The Structure of Radiation

A discussion of the apparent irreconcilability of the quantum theory with the classical wave theory of radiation (referred to in Ch. V) would require too extensive a digression from the main theme of this book, but one aspect of the problem which is of magnetic interest will be briefly considered. While many phenomena, such as interference, polarization and dispersion, seem to demand some kind of wave theory to explain them adequately, many others suggest strongly that radiation is propagated in localized bundles of energy, which may be called " quants." If a quant is characterized by electric and magnetic vectors, the time variation of these may be supposed to give the quant a frequency, their relative magnitudes and directions defining its " phase," and state of polarization. Much of the wave terminology may, in fact, be applied to quants, though this, of course, does not enable an explanation of interference to be obtained.

On the classical electromagnetic wave theory, the energy lost by a radiating system appears in the radiation. Moreover, in complete accord with electromagnetic theory, and relativity, experiments on the pressure of radiation have shown it to be statistically true that absorption of radiant energy $\triangle E$ is associated with transfer of momentum $\triangle E/c$. According to modern views, emission and absorption take place in quanta $h\nu$, and it seems difficult to escape the conclusion that these processes are associated with transfer of momentum $h\nu/c$. For a large number of transition processes there is certainly a statistical conservation of energy and momentum, but it has been suggested, notably by Bohr, Kramers and Slater, that conservation laws may not hold for individual transitions. There is, however, a strong a priori probability that there is conservation in each complete process, and there is no direct evidence of any breakdown. The most direct experiments that have been devised up to the present, although perhaps not absolutely conclusive, strongly support the validity of the conservation principles, as applied to individual processes. In particular may be mentioned investigations on the direction of recoil of electrons due to mono-electronic scattering, and on their ranges, carried out by Compton and others, using the Wilson cloud-chamber method; and the work of Bothe and Geiger, which indicates that the scattering of the " quant " and the recoil of the electron occur simultaneously. If there is conservation of energy and momentum in individual transitions, it may be shown that radiation must be regarded as propagated by linearly directed quants; and further evidence may be brought forward in favour of the view that these quants are spatially localized longitudinally as well as laterally. The problem of explaining interference in terms of quants then arises, and although it is as yet unsolved, it must be remembered that a wave theory is quite unable to account for those phenomena which a quant theory at once renders intelligible.

Adopting the quant picture, and assuming conservation, it is at once possible to link up some of the characteristics of the quant with the changes which occur in the material system on emission or absorption, although the exact nature of the processes is unknown. Thus an atom in which an emission transition occurs loses energy and momentum which appear in the quant. Similarly, any change in the angular momentum of the atom must result in the radiated quant possessing angular momentum, and following Rubinowicz, Sommerfeld and Bohr, this may be regarded as determinative of the state of polarization of the radiation. On the classical theory (as discussed in Ch. X, sect. 1), the total change in the angular momentum $\triangle P$ in the radiation field associated with a vibrating electron is related to the change in energy $\triangle E$ due to emission or absorption in a manner which varies with the mode of vibration of the electron from

$$\triangle P = \frac{\triangle E}{2\pi\nu}$$

for a circularly vibrating electron to

$$\triangle P = 0$$

for a linearly vibrating electron. Carrying this over to the quantum theory, in which ΔE must be put equal to $h\nu$, it is supposed that the angular momentum associated with a quantum may vary from $h/2\pi$ (the unit) to 0. The former may be supposed to correspond to circularly, the latter to linearly polarized light. The observed polarization of the light emitted according to the classical theory by a rotating electron would vary with the direction of observation, and correspondingly it must be supposed that the polarization associated with quants whose emission involves unit change in the angular momentum of an atom varies according to the direction of emission.

It is from the study of the Zeeman effect that the most precise information may be derived as to the relation between the character of the transition and the state of polarization of the emitted radiation. In a magnetic field transitions normally occur (subject to the restrictions $\Delta k = \pm 1$, $\Delta j \not> 1$) for which $\Delta m = 0$ or ± 1, the former corresponding to linearly polarized radiation, and the latter to circularly polarized. Although the circularly polarized radiation may be observed as elliptically or linearly polarized according to the direction of observation, the rather surprising fact seems to emerge that radiation is not emitted corresponding to that which, classically, an electron moving in an ellipse would produce. Since quants cannot be supposed to superpose like waves, it would seem that there must be quants of two essentially distinct types, corresponding to circular ($\Delta m = \pm 1$) and linear ($\Delta m = 0$) polarization. Although the magnetic quantum number m is usually treated as giving the resolved component of the angular momentum j in the field direction (in the usual units), this identification, as has been pointed out, can only be regarded as tentative. On the other hand, there is direct experimental support for the view that the mg values do give the resolved magnetic moments of the atom. It would therefore seem possible to associate with a quant a magnetic moment whose resolved value, in the field direction, is equal to Δmg. Δmg may have values from 0 upwards. For the six magnetic components of the sodium D_2 line, for example, $\Delta mg = \pm \frac{1}{3}$, ± 1, $\pm \frac{5}{3}$. These numbers give the minimum values of the magnetic moment associated with the quants, though not necessarily the maximum. The point which it is desired to emphasize is that, if a quant picture is adopted, it is possible to associate with a quant not only an angular, but also a magnetic moment, and that one component of the magnetic moment may be definitely determined.

The attribution of a magnetic moment to a quant is illustrative of a point of view which may seem highly speculative, but the fact that the phenomena involved cannot in any case be correlated by a wave theory perhaps justifies such speculations. It would be unfruitful to follow them up further at present. It does, however, seem that the attempt to link up "quant" properties with transition characteristics may be of some value, possibly positive and constructive, but if not, in indicating in a different form the essential nature of fundamental difficulties.

4. Summary and Conclusion

The study of magnetism illustrates clearly how closely interwoven are the different branches of science. In this book it has only been possible to discuss a few of the phenomena in which magnetism plays a part. The directness with which the phenomena could be brought into relation with atomic and molecular structure has been the guide in selection and length of treatment. Even within the narrower range, and although many aspects have been very inadequately dealt with, there has been a great variety and wealth of material for consideration, and it seems desirable to summarize as briefly as possible some of the leading motives of the theme.

From the time when men first wondered at the strange properties of the magnet stone, magnetism was for long studied as an independent science. Simple laws were gradually discovered which enabled many of the phenomena to be readily interpreted. A brilliant series of experimental researches brought to light the connection between electricity and magnetism (I). On the basis of these was built up the classical electromagnetic theory, which was later modified and refined by the introduction of the conception of electrons. A place was ready for the experimentally discovered electron with its unique charge, and theory of the electric and magnetic properties of electrons was developed (II). In the earlier work, methods for investigating the magnetic properties of substances were devised, and it was found that there were the three classes of ferro-, para- and dia-magnetics, each with special characteristics (III). It had been recognized that magnetism must be interpreted as an atomic phenomenon, but an epoch is marked by the explanation of the different types of magnetic behaviour in terms of an electronic theory of atomic structure. While diamagnetism is common to all matter, para- and ferro-magnetism involve the existence of atomic carriers, with a resultant magnetic moment such as would arise from unbalanced electronic orbits. In details there were difficulties, partly in connection with the stability of the systems assumed, partly in connection with the orientation of paramagnetic carriers, and partly in connection with the large internal fields which must be assumed to exist in ferromagnetics (IV). The first of these, while not removed, was put on an entirely different footing by the quantum theory of atomic structure. The assumption that interchange of energy between matter and free space could only occur in quanta was found not only to account for the spectral energy distribution of temperature radiation, in connection with which classical theory broke down completely, but also to lead to consequences which were abundantly verified by experiment. As applied to atomic structure, a second assumption, or postulate, had to be made in the quantum theory—that only certain stable " stationary " non-radiating states were possible for the electrons in the atom, rotating about a nucleus, these states being fixed by quantum conditions. Later developments have led to a conception of atomic structure, which, though indefinite and imperfect in many details, as a whole is remarkably complete and coherent. A much more precise theoretical interpretation of atomic magnetic properties becomes possible, and the question of orientation of carriers in a magnetic field assumes an entirely new significance, for, according to the theory, in a magnetic field, ideally, only certain discrete orientations can occur (V).

While the quantum theory was being developed many accurate determinations of magnetic susceptibilities were made. Atomic moments were deduced and expressed as multiples of an experimental unit magneton (VI). The experimental magneton is some five times smaller than the quantum unit, but reinterpretation on the lines suggested by the quantum theory shows that the results can be co-ordinated into a harmonious scheme. Difficulties, however, are still encountered in connection with the internal fields in ferromagnetics and most paramagnetics. These may be linked up with phenomena of " residual paramagnetism " (VII).

If the mechanical and magnetic moments of paramagnetic carriers depend primarily on electronic motion, the theoretical ratio between them can be readily calculated. It may also be deduced with apparent directness from experiments on the gyromagnetic effect. The experimental ratio, however, is half the theoretical ratio. No satisfactory explanation of this outstanding gyromagnetic anomaly has yet been given (VIII).

The quantum-theory predictions as to the magnitude of the unit magneton and the spatial orientation of electron orbits have been strikingly confirmed by experiments on the magnetic deviation of atomic rays. The difficulties in connection with the mechanism by which orientation is brought about become particularly prominent (IX). These investigations provide a direct experimental basis for the quantum theory of the Zeeman effect, and the multiplet structure of spectral lines. Many of the simpler phenomena may be interpreted in a natural and straightforward manner, but others can only be correlated by formal schemes. Magnetic moments of atoms deduced spectroscopically may be brought into relation with those found from susceptibility measurements. The intensity relations of lines of multiplets are in close agreement with rules suggested by the quantum theory, but the relative and absolute values of multiplet intervals have not been satisfactorily accounted for. Neither the relativity nor the magnetic interpretation is adequate, and a physically significant fusion of the two has yet to be found (X). While many magneto-optical effects still seem to be most simply approached from the standpoint of the classical wave theory, the influence of a magnetic field on the polarization of resonance radiation may be linked up directly with the Zeeman effect, and may largely be explained on a quantum basis. The phenomena are of particular interest, as being of a type to which the quantum and wave theories may both be applied to a certain extent, and further investigations may reveal some of the reasons for their individual limitations. In particular, the range of validity of the quantum orientation rules under limiting conditions as to field strengths may be tested. Some of the anomalies found may have an important bearing on the general theory of radiation (XI).

Diamagnetism is largely amenable to classical treatment, and that the usual theory is correct in essentials is shown by the values found for diamagnetic susceptibilities. In gases, changes in molecular susceptibility with pressure and field are found, which seem to indicate that some form of " diamagnetic orientation " can occur. In solid diamagnetics there is considerable evidence for the existence of internal fields of a similar nature to those in paramagnetics (XII).

Magneto-mechanical effects are closely connected with crystalline structure. It seems that the type of linkage between atoms in a crystalline edifice is largely determinative of the internal fields, which also play a part in galvano- and thermo-magnetic phenomena ; these, in their great variety, are quite inexplicable on any simple free-electron theory. Investigations on the magneto-caloric effect support the view that there are powerful internal fields in ferromagnetics, though their precise nature remains problematical (XIII).

With the information derivable as to elementary moments from magneto-chemical measurements, spectroscopy, and the magnetic deviation of atomic rays, it is possible to make a survey of the magnetic properties of atoms and ions as grouped in a periodic classification. From the diamagnetic susceptibilities of the inert gases, conclusions may be drawn as to the structure of their atoms; and, as further electrons are added to these, sequential magnetic relations are found of a kind which, on the whole, support strongly the general quantum theory of atomic structure (XIV). Quantum ideas may also be applied to elucidate molecular magnetic properties, and while the theories are yet vague, they lead to a number of fairly definite conclusions. Molecules, like atoms, must be treated as quantum dynamical systems; and crystals represent a further stage in the upbuilding processes (XV).

A few general problems—as to atomic stability, weak quantization, and the structure of radiation—have finally been briefly considered (XVI).

Gaps in experiment and inadequacies in theory have constantly been encountered and emphasized. Perhaps the outstanding magnetic problems are those connected with the gyromagnetic anomaly, the mechanism of orientation, and the nature of internal fields. The first is related to the difficulty of giving a physically significant treatment of the Zeeman effect; the second to the super-mechanical tendency of systems to assume quantum stationary states; and the third to the general problem of crystal structure and stability.

Although there are the many difficulties, it is with clearer vision that there has come the clearer realization of the existence of regions which are obscure; for there has undoubtedly been an enormous advance in the understanding of magnetism in the course even of the last few years. The outlook which has been adopted in this book may eventually be completely changed, and the phenomena may be seen and interpreted anew as part of a simpler and more satisfying design. But the quantum theory, even in its present form, will have had a lasting value for the part it has played in enabling that design to be built up. A vast realm lies open before the creative explorers of science, the many and the few, who all, as artists, add to the wonder and beauty of the world by their revelation of its significance.

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